

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 July 2009 (23.07.2009)

PCT

(10) International Publication Number  
WO 2009/091437 A1

- (51) International Patent Classification:  
**B01D 53/50** (2006.01)    **C01B 31/20** (2006.01)  
**B01D 53/62** (2006.01)    **F23J 15/04** (2006.01)  
**B01D 53/75** (2006.01)
- (21) International Application Number:  
PCT/US2008/081998
- (22) International Filing Date: 31 October 2008 (31.10.2008)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
61/021,973    18 January 2008 (18.01.2008)    US  
PCT/US2008/062174    1 May 2008 (01.05.2008)    US  
PCT/US2008/063265    9 May 2008 (09.05.2008)    US  
PCT/US2008/069771    11 July 2008 (11.07.2008)    US  
61/084,524    29 July 2008 (29.07.2008)    US  
PCT/US2008/074052    22 August 2008 (22.08.2008)    US  
PCT/US2008/075983    11 September 2008 (11.09.2008)    US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

[Continued on next page]

(54) Title: REMOVAL OF CARBON DIOXIDE FROM A FLUE GAS STREAM

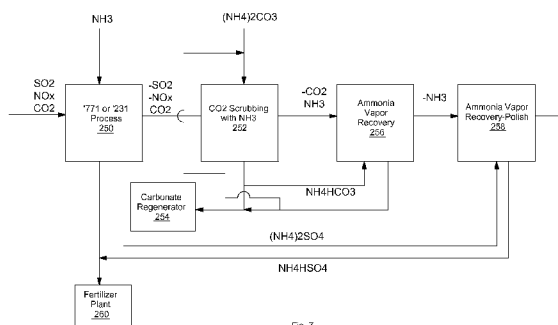


Fig. 7

(57) Abstract: A method and apparatus for removing carbon dioxide and other pollutants from a gas stream having components that work synergistically. The invention includes an ammonia based scrubbing solution for SO<sub>2</sub> scrubbing; an SO<sub>2</sub> absorption section (250) to create contact between the flue gas and the ammonia based scrubbing solution to remove SO<sub>2</sub> from the flue gas; a wet electrostatic precipitator to remove aerosols and fine particulate matter from the flue gas; a regenerable carbonate scrubbing solution for CO<sub>2</sub> scrubbing, - a CO<sub>2</sub> absorption section (252) for removal of CO<sub>2</sub> adapted to create contact between the flue gas and the scrubbing solution and which operates at a temperature between 32 and 66 degrees C and including mass transfer apparatus and liquid distribution apparatus to provide the gas and liquid contact; an ammonia absorption section (256, 258) to capture ammonia vapor which creates contact between at least some of the liquid leaving the SO<sub>2</sub> absorption section and the gas leaving the CO<sub>2</sub> absorption section and return ammonia rich liquid leaving the CO<sub>2</sub> absorption section to the SO<sub>2</sub> absorption section for use in SO<sub>2</sub> capture; a regeneration tower (254) to release CO<sub>2</sub> from the scrubbing solution, the regeneration tower comprising: packing for mass transfer; apparatus for allowing the spent scrubbing solution to be introduced at elevated temperature; and apparatus for introducing heat to the regenerator tower, - a controller for controlling the absorption and regeneration system parameters selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and a heat recovery device to recover energy during the heating and cooling of the absorption and regeneration column liquids.

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AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— *of inventorship (Rule 4.17(iv))*

**(84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH,

**Published:**

— *with international search report*

## REMOVAL OF CARBON DIOXIDE FROM A FLUE GAS STREAM

### BACKGROUND

Most of the energy used in the world today is derived from the combustion of hydrocarbons, such as coal, oil, and natural gas. In addition to carbon and hydrogen, these fuels contain water and contaminants like sulfur, mercury, and ash. Nitrogen oxides are also formed and emitted as a result of combustion. Because of the harmful effects of these substances on human health and the environment, stringent regulations have been put in place to require power plants to use pollution control equipment. Now, carbon dioxide emissions from these plants have been targeted for similarly strict regulations because it is a greenhouse gas tied to global warming.

Others have developed pollution control equipment that treats one or perhaps two of the listed pollutants separately. They are expensive because they must treat high volumes of flue gas and low concentrations of pollutants. They have discreet inputs and outputs. Their use has a significant impact on the total cost of energy. The additional need for carbon dioxide removal makes the problem especially acute. What is needed, therefore, is a method and apparatus for removing carbon dioxide and other pollutants from a gas stream having components that work synergistically.

### SUMMARY

The invention is a method and apparatus for removing carbon dioxide and other pollutants from a gas stream having components that work synergistically. The invention comprises an ammonia based scrubbing solution for SO<sub>2</sub> scrubbing; an SO<sub>2</sub> absorption section to create contact between the flue gas and the ammonia based scrubbing solution to remove SO<sub>2</sub> from the flue gas; a wet electrostatic precipitator to remove aerosols and fine particulate matter from the flue gas; a regenerable carbonate scrubbing solution for CO<sub>2</sub> scrubbing; a CO<sub>2</sub> absorption section for removal of CO<sub>2</sub> adapted to create contact between the flue gas and the scrubbing solution and which operates at a temperature between 32 and 66 degrees C and comprising mass transfer means and liquid distribution means to provide the gas and liquid contact; an ammonia absorption section to capture ammonia vapor

which creates contact between at least some of the liquid leaving the SO<sub>2</sub> absorption section and the gas leaving the CO<sub>2</sub> absorption section and return ammonia rich liquid leaving the CO<sub>2</sub> absorption section to the SO<sub>2</sub> absorption section for use in SO<sub>2</sub> capture; a regeneration tower to release CO<sub>2</sub> from the scrubbing solution, the regeneration tower comprising: packing for mass transfer; means for allowing the spent scrubbing solution to be introduced at elevated temperature; and means for introducing heat to the regenerator tower; a controller for controlling the absorption and regeneration system parameters selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and a heat recovery device to recover energy during the heating and cooling of the absorption and regeneration column liquids. These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, claims, and accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a process flow diagram of a basic thermal swing absorption process.

Fig. 2 is a schematic diagram of the process of the present invention synergistically coupled with another multi-pollutant control technology.

Fig. 3 is a chart showing equilibrium ammonia and CO<sub>2</sub> vapor pressure under absorber conditions.

Fig. 4 is a chart showing the effect of temperature on solution regeneration.

Fig. 5 is a chart showing the effect of temperature on CO<sub>2</sub> absorption and ammonia release rates.

Fig. 6 is a chart of the steady state absorption performance in a lab scale absorption / regeneration system.

Fig. 7 is a flow chart of one embodiment of the method of the present invention used with multi-pollutant control technology.

Fig. 8 is an arrangement of an apparatus according to the method shown in Fig. 7.

Fig. 8A is a detailed schematic of a regenerator with associated equipment.

Fig. 9 is an arrangement of an apparatus according to another embodiment of the present invention.

Fig. 10 is a process flow chart of the embodiment of Fig. 9.

Fig. 11 is an arrangement of another embodiment of the present invention.

Fig. 12 is a process flow chart of another embodiment of the present invention.

Fig. 13 is an arrangement of an apparatus according to the embodiment of Fig. 12.

Fig. 14 is a process flow chart of another embodiment of the present invention.

Fig. 15 is an arrangement of an apparatus according to the embodiment of Fig. 14.

Fig. 16 is an arrangement of an apparatus according to another embodiment of the present invention.

Fig. 17 is a process flow chart of the embodiment of Fig. 16.

Fig. 18 shows the absorption spectra of carbonate and bicarbonate.

Fig. 19 is a process flow chart of another embodiment of the present invention.

Fig. 20 is a process flow chart showing a different application of the embodiment of Fig. 19.

Fig. 21 is an arrangement of a product gas clean up apparatus according to another embodiment of the present invention.

Fig. 22 is a process flow diagram of the overall process of the invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

### **Introduction**

While CO<sub>2</sub> emissions from power plants are currently unregulated, there is a growing consensus that standards limiting CO<sub>2</sub> emissions are likely to be promulgated soon. Carbon dioxide emissions from the electric power sector account for 40 percent of total U.S. energy-related CO<sub>2</sub> emissions. With 50 percent of U.S. electricity generated from coal and many new coal-fired electric generating plants in the planning, permitting, or construction stages, it is becoming increasingly important that CO<sub>2</sub> capture solutions are developed which are suitable for the existing fleet of coal-burning power plants, as well as for planned, new capacity. Today, limited CO<sub>2</sub> capture technologies are commercially available for use on coal-fired power plants, and none has been deployed at the scale of the typical base loaded plant. In

addition, existing CO<sub>2</sub> capture solutions have capital and operating costs that are considered uneconomical for conventional coal-fired power plants.

The present invention includes a CO<sub>2</sub> capture process that can be applied to both existing and new coal-fired power plants. The process is being designed as an add-on system that could be deployed when needed and is particularly advantageous for sites where ammonia-based scrubbing is employed.

The present invention also includes a scrubbing process that uses an ammonia-based solution to capture CO<sub>2</sub> from flue gas. The CO<sub>2</sub> capture takes place after NO<sub>x</sub>, SO<sub>2</sub>, Hg and fine particulate matter capture is accomplished in other air pollution control systems, if provided. Once CO<sub>2</sub> is absorbed, the resulting solution is regenerated to release it. In addition to CO<sub>2</sub>, NH<sub>3</sub> is released during regeneration. It is recovered and returned to the scrubbing process, and the product CO<sub>2</sub> is dried and compressed into a form that is sequestration ready. Ammonia is not consumed in the scrubbing process, and no separate by-product is created.

Extensive laboratory testing on CO<sub>2</sub> capture using the process of the present invention has been performed. The testing has demonstrated steady-state capture/regeneration operation with 90 percent CO<sub>2</sub> removal under conditions comparable to a commercial-scale absorber. Based on these results, a pilot plant is being built and commercial scale units are being designed.

## **Technology Overview**

Post combustion carbon dioxide (CO<sub>2</sub>) capture from coal-fired power plants takes place downstream of any employed sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and mercury (Hg) removal process steps. When integrated with other multi-pollutant control processes, CO<sub>2</sub> capture takes place after the SO<sub>2</sub>, NO<sub>x</sub>, mercury, and fine particulate matter is removed. Although the SO<sub>2</sub> capture efficiency of other processes can be effective (typically greater than 98%), supplemental SO<sub>2</sub> removal would be advantageous to a rate of 99.5% or more. This is because SO<sub>2</sub> must be removed in the CO<sub>2</sub> process as a waste, which increases the cost.

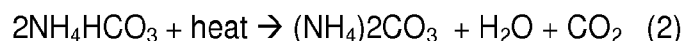
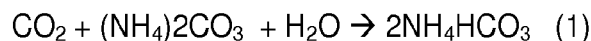
The process of the present invention uses an ammonia-based solution to absorb CO<sub>2</sub> from flue gas. Once the CO<sub>2</sub> is absorbed, the solution containing CO<sub>2</sub> is regenerated through heating to release the captured carbon dioxide. Ammonia and water vapor are also released during regeneration, though these are recovered and returned to the absorbing solution. The product CO<sub>2</sub> is then in a form that is ready

for compression, pipeline transport and sequestration. The process of the present invention does not consume ammonia and no separate by-product is created by a system according to the present invention.

The process of the present invention is a thermal swing absorption (TSA) process for CO<sub>2</sub> capture. CO<sub>2</sub> absorption into the ammonia-based solvent takes place at low temperature, similar to temperatures achieved in wet flue gas scrubbing systems. The solvent is then heated to release the CO<sub>2</sub>. The process is similar to other CO<sub>2</sub> capture technologies such as amine-based processes. Common to thermal swing absorption processes are the following key parts, which are depicted in Fig. 1.

CO<sub>2</sub> is absorbed in a solution through flue gas–solution contact in an absorber 102. The solution is heated by a heating means 104 for regeneration. CO<sub>2</sub> is released from the heated solution in a regenerator 106. The solution is cooled for reuse.

In the process of the present invention, CO<sub>2</sub> in the flue gas is scrubbed with an aqueous solution containing ammonium carbonate, forming ammonium bicarbonate as shown in reaction 1. The ammonium bicarbonate solution is then removed from the flue gas stream and heated, reversing the scrubbing reaction to release CO<sub>2</sub> while forming ammonium carbonate (reaction 2).



CO<sub>2</sub> released in reaction 2 is compressed for sequestration while the ammonium carbonate solution is returned to the scrubber for reuse.

The major advantage of an ammonia-based scrubbing solution is the reduced energy of reactions (1) and (2) when compared to amine-based and other CO<sub>2</sub> capture processes. This substantially reduces the energy consumption associated with solution regeneration. However, ammonia's volatility requires control of ammonia vapor released to the flue gas during CO<sub>2</sub> scrubbing, and to the product gas during solution regeneration. The process of the present invention captures ammonia released to the flue gas during CO<sub>2</sub> scrubbing, reducing the concentration to less than 5 ppmv, and also recovers ammonia from the CO<sub>2</sub> product gas, after regeneration, for reuse.

An illustration of how the process is integrated with other another multi-pollutant control systems is shown in Fig. 2 below. This example uses the system

disclosed in U.S. Pat No. 6,605,263 (the '263 process) that has a barrier discharge reactor, wet scrubber and wet electrostatic precipitator to remove high levels of NO<sub>x</sub>, SO<sub>2</sub>, mercury, and fine particulate matter. The wet scrubber uses aqueous ammonia for SO<sub>2</sub> scrubbing, producing ammonium sulfate fertilizer co-product.

Managing ammonia vapor, which is released in the scrubbing and regeneration steps of the process of the present invention is an important factor in the environmental impact and process economics of using ammonia for CO<sub>2</sub> capture. Figure 2 shows how ammonia vapor 108 released from the scrubber 110 is controlled using scrubbing liquor from the '263 process Upper Loop 112. In a '263 system without the CO<sub>2</sub> process of the present invention, ammonia is added to the upper loop scrubbing liquor. This is done after the liquor is withdrawn from the absorber, and before returning the liquor to the upper loop packed section. When CO<sub>2</sub> scrubbing is employed, the bulk of the ammonia addition to the '263 process upper loop is accomplished by contacting the upper loop solution with flue gas leaving the CO<sub>2</sub> scrubbing section. The contact takes place in the Ammonia Capture section of the present process absorber tower. The now ammonia rich liquid from the Ammonia Capture section is collected in the Ammonia Capture tank and pumped back to the '263 process Upper Loop for scrubbing of SO<sub>2</sub> from the flue gas. In this configuration, ammonia that would have been added directly to the '263 process is instead added to the CO<sub>2</sub> Scrubbing section of the present process absorber, then captured in the Ammonia Capture section and carried to the '263 absorber.

### **Comparison to Amine-Based CO<sub>2</sub> Capture Systems**

Ammonia scrubbing of CO<sub>2</sub> potentially offers several advantages over the commercially available amine process for CO<sub>2</sub> capture from coal-fired power plants. According to research conducted by the DOE-NETL and others on the use of aqua ammonia for absorption of CO<sub>2</sub>:

1. The traditional monoethanolamine (MEA) process for CO<sub>2</sub> removal has disadvantages of low CO<sub>2</sub> loading capacity (kg CO<sub>2</sub> absorbed per kg absorbent); high equipment corrosion rate; amine degradation by SO<sub>2</sub>, NO<sub>2</sub>, HCl, HF and O<sub>2</sub> in the flue gas, which requires a high absorbent makeup rate); and high energy consumption during absorbent regeneration.
2. By comparison, aqua ammonia has higher loading capacity; does not pose a



corrosion problem; does not degrade in a flue gas environment, minimizing absorbent makeup; requires much less energy to regenerate; and costs much less than MEA. Specifically, the aqua ammonia process compared to MEA:

- Has higher CO<sub>2</sub> absorption capacity;
- Requires substantially less heat to release CO<sub>2</sub> and regenerate absorbent; and
- Has lower reagent makeup costs.

3. Another major benefit is that removal of other pollutants (principally SO<sub>2</sub> and NO<sub>x</sub>) could be integrated with the aqua ammonia process for CO<sub>2</sub> removal (i.e. using the '263 multi-pollutant control technology). Due to the requirements of the MEA process, very low SO<sub>2</sub> flue gas is a necessary input (less than 10 ppm). Since most commercially available SO<sub>2</sub> scrubbing systems are not efficient enough to provide this low SO<sub>2</sub> flue gas to the CO<sub>2</sub> scrubbing system (especially on existing units with already-deployed SO<sub>2</sub> scrubbers), an auxiliary SO<sub>2</sub> scrubbing system would be needed, increasing the CO<sub>2</sub> capture system capital cost.

### **Laboratory Testing Results**

Initial laboratory testing of the CO<sub>2</sub> absorption process demonstrated 90 percent CO<sub>2</sub> removal under conditions comparable to a commercial-scale absorber: temperature 54 degrees C; residence time 4-5 seconds; L/G 65 gpm/kacfm; flue gas containing CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>.

Based on these promising initial results, extensive laboratory testing has been conducted to establish the effectiveness of the process of the present invention for CO<sub>2</sub> capture.

The laboratory testing has consisted of: 1) verification of analytical techniques for measurement of the composition of gas and liquid streams, 2) equilibrium testing and modeling to establish limits for absorption and regeneration, 3) absorption rate testing to predict the mass transfer requirements for CO<sub>2</sub> absorption under commercial conditions (gas velocity, liquid to gas ratio) and in commercial mass transfer media (packing), 4) regeneration testing to establish optimal conditions for CO<sub>2</sub> release, 5) ammonia recovery from the regenerator off-gas and 6) combined absorption and regeneration in a cycling system that operates under steady state conditions.

Equilibrium testing under absorption conditions has been used to define the solution composition, temperature and flow rate that maintains driving force for CO<sub>2</sub> capture throughout the absorber. It also has established the limit on ammonia vapor release and CO<sub>2</sub> absorption capacity.

Figure 3 shows the normalized ammonia and CO<sub>2</sub> vapor pressure as a function of solution pH for three temperatures. As is expected, the ammonia vapor pressure increases with increasing pH and temperature, while the CO<sub>2</sub> vapor pressure decreases with increasing pH, and increases with increasing temperature. Similar equilibrium testing under regeneration conditions establishes the temperature and pressure for solution regeneration and the quantity of ammonia and water vapor released relative to the CO<sub>2</sub> release.

This is shown in Figure 4, where it can be seen that increasing regeneration temperature increases the partial pressure of water vapor, CO<sub>2</sub> and NH<sub>3</sub>, and therefore the total pressure. However, the figure also shows that above the design temperature the increase in water vapor partial pressure with temperature is greater than that of CO<sub>2</sub>, increasing the relative concentration of water vapor to CO<sub>2</sub>. The design regeneration temperature is chosen based on minimizing the energy input to the regenerator in conjunction with minimizing the compression energy required to get to final system pressure.

Absorption rate testing has been conducted in a 10 cm diameter laboratory packed tower absorber. Performance of the laboratory absorber for SO<sub>2</sub> and NO<sub>2</sub> scrubbing in the '263 process has been correlated to the performance of commercial demonstration scale 5.2 meter and 0.76 meter diameter scrubbing towers. The laboratory absorber system uses flue gas from propane combustion, into which SO<sub>2</sub>, NO<sub>x</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, HCl and Hg are added as needed to simulate the composition of coal combustion produced flue gas. The testing conducted included the effect of packing height, gas flow rate, solution composition and temperature on CO<sub>2</sub> removal and ammonia vapor release.

An example from the testing (Figure 5) shows the normalized effect of temperature on CO<sub>2</sub> absorption and ammonia vapor release rates from the CO<sub>2</sub> scrubber for a given solution composition.

It can be seen that although the ammonia vapor release rate decreases with decreasing temperature, the CO<sub>2</sub> absorption rate also decreases. The design temperature (DT) depicted in the figure is the scrubbing temperature that maximizes

the CO<sub>2</sub> scrubbing rate with an ammonia vapor release rate from the process of the present invention that can be controlled to less than 5 ppm.

Testing in a lab scale regenerator establishes the impact of temperature, pressure and residence time on the release of CO<sub>2</sub> from the absorbing solution. This testing also establishes the energy requirements for regeneration and the gas flow rates of ammonia and water. The energy input is compared to literature values to verify the regeneration reaction mechanism.

Shown in Figure 6 are the inlet and outlet CO<sub>2</sub> concentrations, and the CO<sub>2</sub> removal for one set of operating conditions. The figure shows performance for approximately 1 hour after steady state was achieved. The solution capacity for CO<sub>2</sub> during the test represented by the figure was 0.03 lbm-CO<sub>2</sub> per lbm of absorbing solution, at a liquid to gas ratio of 50 gpm/kacfm.

Table 1 presents test results from the laboratory system for CO<sub>2</sub> absorption and solution regeneration. Concentrations of the gas entering and exiting the CO<sub>2</sub> absorber and exiting the regenerator are provided along with absorber and regenerator pH.

Table 1: CO<sub>2</sub> Absorption and Regeneration

Stream	Parameter	Units	Test 1	Test 2	Test 3	Test 4
<b>ABSORBER</b>						
Gas Inlet to CO <sub>2</sub> Absorber	Flue Gas Temp	(F)	120	120	120	120
	Pressure	(psia)	14.7	14.7	14.7	14.7
	Gas Flow Rate	(L/min)	3.0	3.0	3.0	3.0
	CO <sub>2</sub> Concentration	(%)	11.7	11.7	11.7	11.7
Gas Exit from CO <sub>2</sub> Absorber	Temperature	(F)	115	112	110	109
	[CO <sub>2</sub> ]	(%)	0.7	1.3	0.8	0.7
	[NH <sub>3</sub> ]	(%)		0.34	0.35	0.31
	[H <sub>2</sub> O]	(%)		19	18	24
Lean Liquid Into Absorber	Lean Liquid Temperature	(F)	129	126	125	124
	Lean Liquid Flow rate	(cc/min)	25	25	25	25
	pH		10.25	10.18	10.22	10.15
	Specific Gravity total [CO <sub>3</sub> <sup>-2</sup> ]	(wt%)	1.109	1.099	1.099	1.105
			6.8	6.6	6.5	6.6
<b>REGENERATOR</b>						
Rich Liquid Into Regenerator	Rich Liquid Temperature	(F)	220	235	235	236
	Rich Liquid Flow rate	(cc/min)	25	25	25	25
	total [CO <sub>3</sub> <sup>-2</sup> ]	(wt%)	9.9	9.9	10.1	10.4
	pH		9.04	8.97	8.91	8.98
Liquid Out of Reboiler	Temperature	(F)	290	300	300	280
Regen Gas Outlet	Temperature	(F)	223	220	226	225

Pressure	(psia)	30.2	29.7	32.1	32.2
CO <sub>2</sub>	(%)	43	44	51.5	46
NH <sub>3</sub>	(%)	0.6	2.8	2.5	4
H <sub>2</sub> O	(%)	56	53.2	46	50

**Performance Comparison of the Present Invention**

An analysis of the energy consumption of an present process, and its impact on power plant output has been made based on the laboratory results obtained to date. Shown in Table 2 is an estimate of performance comparing the process of the present invention and an MEA system retrofit on an existing coal fired power plant, obtaining 90% CO<sub>2</sub> removal. Data for the base plant and MEA process were obtained from “Carbon Dioxide Capture from Existing Coal-Fired Power Plants”, DOE/NETL-401/110907, Revision Date, November 2007. Shown in the table is the gross and net power output for the base plant with wet flue gas desulfurization (WFGD), an MEA process with enhanced WFGD, and the process of the present invention using the ammonia based ‘263 process for SO<sub>2</sub> removal. The analyses show that the power plant gross output is reduced from 463 MW to 449 MW with installation of the present process, and to 388 MW with an MEA system. The analysis also shows that the plant’s net output is reduced by 16% when using the process of the present invention for CO<sub>2</sub> capture, and by 30% when an MEA system is used.

	Base Plant w/o CO <sub>2</sub> Capture	MEA w/ enhanced WFGD	Present process with ‘263 process
Gross Output (MW)	463	388	449
Balance of Plant (MW)	30	30	30
CO <sub>2</sub> Capture and Compression (MW)		55	57
Net Output (MW)	434	303	362
% Loss from Base Plant	-	30%	16%

A comparison of the energy usage in MEA and process of the present invention for CO<sub>2</sub> capture and regeneration is shown in Table 3. The process energy

consumption can be segregated into three categories: 1) sensible heat, 2) reaction energy and 3) stripping steam. The sensible heat component is the energy needed to raise the temperature of the scrubbing solution to the regenerator temperature and which cannot be recovered. Reaction energy is simply the heat of reaction for absorption of CO<sub>2</sub>, and stripping steam is the energy associated with the steam needed or produced during the regeneration process. Table 3 shows that the energy requirement of the present process is less than that of MEA in each category. Data for the MEA system is taken from "An Economic Scoping Study for CO<sub>2</sub> Capture Using Aqueous Ammonia", DOE/NETL Final Report, Revised, February 2005. The table shows that the present process total energy requirement of 493 Btu/lb-CO<sub>2</sub> is 27% of the MEA energy requirement of 1,812 Btu/lb-CO<sub>2</sub>.

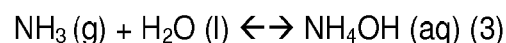
	MEA	Present Process
Sensible Heat	372	128
Reaction Energy	825	277
Stripping Steam	615	88
Total Energy	1,812	493

### **SO<sub>2</sub> Removal Process / '263 Process**

Removing SO<sub>2</sub> before the CO<sub>2</sub> removal process of the present invention is highly desirable due to the impact on cost of CO<sub>2</sub> removal in the presence of SO<sub>2</sub>. Nonetheless, a review of the chemistry involved is helpful to appreciate the synergies of a combined system using ammonia. A system that carries out the process is shown as Fig. 2 item 120. Although one tower is shown, any number of towers or reactors could be used.

### **Ammonia Chemistry**

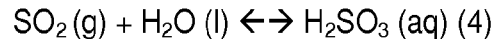
If anhydrous ammonia is used, Reaction 3 shows the reaction for dissolving pure ammonia (NH<sub>3</sub>) in water (H<sub>2</sub>O) to form aqueous ammonia (NH<sub>4</sub>OH).



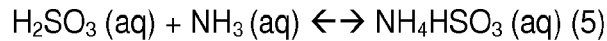
For each molecule of sulfur dioxide (SO<sub>2</sub>) absorbed, two molecules of NH<sub>4</sub>OH are required.

### '263 Chemistry

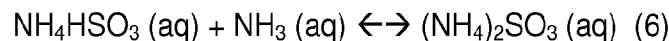
In the '263 absorber, SO<sub>2</sub> in the flue gas is absorbed and dissolves in the absorber water as shown in Reaction 4. The result is sulfurous acid (H<sub>2</sub>SO<sub>3</sub>).



Reaction 4 is reversible; the SO<sub>2</sub> can come back out of the solution and re-enter the flue gas unless the H<sub>2</sub>SO<sub>3</sub> is reacted with another species in solution. In the case of the ECO-SO<sub>2</sub> process, the H<sub>2</sub>SO<sub>3</sub> is reacted with NH<sub>3</sub>. This partial neutralization reaction, shown in Reaction 5, results in the formation of bisulfite (HSO<sub>3</sub><sup>-</sup>).

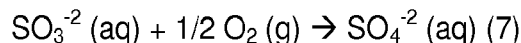


The bisulfite can react with another OH<sup>-</sup> in Reaction 6 to form sulfite (SO<sub>3</sub><sup>-2</sup>).

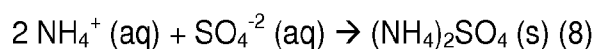


The relative amounts of SO<sub>3</sub><sup>-2</sup>, HSO<sub>3</sub><sup>-</sup> and H<sub>2</sub>SO<sub>3</sub> depend upon the pH of the solution. If the pH goes down, the total amount of these sulfur compounds in solution will decrease and SO<sub>2</sub> will be released back into the flue gas. Adding ammonia increases the pH, so more SO<sub>2</sub> can be absorbed in the same amount of liquid. However, if the pH goes too high, Reaction 3 can go backwards and ammonia is released into the flue gas.

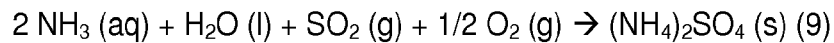
In order to trap the SO<sub>2</sub> in the liquid, the sulfite ion (SO<sub>3</sub><sup>-2</sup>) is converted through oxidation to form sulfate (SO<sub>4</sub><sup>-2</sup>). This is accomplished by blowing air through the sulfite-containing liquid. The oxygen in the air oxidizes the SO<sub>3</sub><sup>-2</sup> to SO<sub>4</sub><sup>-2</sup> as shown in Reaction 7. This reaction is not reversible and the sulfur in the sulfate form cannot re-enter the flue gas.



The ammonium from the aqueous ammonia and the sulfate from the SO<sub>2</sub> eventually become the ammonium sulfate fertilizer, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, which is the primary product from the '263 process. This is shown in Reaction 8.



Reaction 9 is the net overall reaction when you combine Reactions 4 through 8: aqueous ammonia plus SO<sub>2</sub> and oxygen yield ammonium sulfate and some residual water.



If one does not use the '263 process, another NH<sub>3</sub> capture process would have to be used.

### Embodiment 1

One embodiment of a process of the present invention is a method and apparatus for removing carbon dioxide from a gas stream and controlling ammonia vapor comprising the steps of scrubbing the carbon dioxide from the gas stream with an ammonium carbonate solution, thereby producing ammonia vapor and ammonium bicarbonate; removing a portion of the ammonia vapor from the gas stream with ammonium bicarbonate; and polishing the flue gas to achieve an ammonia concentration of less than 10 PPM.

Turning to Fig. 7, flue gas typically contains SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub>. The SO<sub>2</sub> and NO<sub>x</sub> are preferably processed by the method and apparatus disclosed in U.S. Pat. No. 6,605,263, entitled SULFUR DIOXIDE REMOVAL USING AMMONIA, and U.S. Pat. No. 6,936,231, entitled NO<sub>x</sub>, Hg, AND SO<sub>2</sub> REMOVAL USING AMMONIA. These processes will be referred to as the '263 and '231 processes and depicted in the diagram as 250. Although the '263 or '231 processes provide solutions that are some preferred methods for scrubbing NH<sub>3</sub> vapor released during CO<sub>2</sub> scrubbing, as will be shown later in this specification, other processes requiring the addition of ammonia could be used instead of the '263 and '231 processes and would be known to those skilled in the art.

The CO<sub>2</sub> scrubbing process and apparatus can be integral with the apparatus island of the '263 or the '231 process, or it can be in its own tower with ductwork moving flue gas from one tower to the other. Regardless, after either the '263 or '231 process 250, the CO<sub>2</sub> is scrubbed with an ammonium carbonate solution 252. The scrubbing produces ammonia vapor and ammonium bicarbonate, and the scrubbing solution becomes an ammonium carbonate / ammonium bicarbonate solution. A portion of the solution is drawn off to a regeneration step 254.

Another portion of the solution is drawn with the remaining flue gas, having less CO<sub>2</sub>, to the first ammonia vapor recovery step 256. However, it is not expected that the ammonium carbonate solution will be able to recover all of the ammonia released during CO<sub>2</sub> scrubbing. Therefore, a second ammonia capture section 258 is necessary to decrease the NH<sub>3</sub> release to less than 10 ppmv.

The second ammonia step removes or captures any remaining ammonia vapor from the flue gas 258 with solution from the upper loop of either the '263 or '231 process or from the lower loop of the '263 process. The ammonia vapor concentration exiting with the flue gas is <10 ppm. In the '263 and '231 process, the upper loop requires ammonia addition to remove SO<sub>2</sub> and NO<sub>x</sub> and operates with ammonia slip of < 10 ppm. The requirement for ammonia addition to the upper loop of the '263 and '231 process in addition to the ability for it to operate with low ammonia slip would enable the CO<sub>2</sub> scrubbing and '263 or '231 process to operate synergistically without ammonia slip. This step is called the polishing step or NH<sub>3</sub> capture step.

When the CO<sub>2</sub> scrubbing step 252 is used in conjunction with the '263 process, the lower loop solution can be used to remove the remaining NH<sub>3</sub> vapor from the flue gas prior to discharge to the atmosphere. The requirement for ammonia in this section is not as high as for the upper loop of the '263 process and therefore will have a smaller capacity for NH<sub>3</sub> vapor, but the lower pH will be a more efficient NH<sub>3</sub> scrubbing liquid and therefore decrease the amount of mass transfer necessary to capture the ammonia vapor. The output of the '263 and '231 process is (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, which can be collected for turning into fertilizer at a fertilizer plant 260, or can be used in the polishing step 258.

An apparatus according to the present invention is shown in the schematic of Fig. 8. A scrubbing tower 116 is provided as one embodiment, but it can be appreciated that the tower could be divided into several different apparatuses. This figure shows one approach for removing NO<sub>x</sub>, SO<sub>2</sub>, and CO<sub>2</sub> from flue gas through modification of the '263 process, shown collectively as item 202 and comprising a reactor, lower loop 206, upper loop 208, and WESP 210. A section 204 is added to the process whether it be integral to the '771 process island 202 as shown in the figure or a stand alone tower with ductwork moving flue gas from one tower to the other and back. The initial steps of the process are the first steps of the '771 process: (i) convert NO<sub>x</sub> to NO<sub>2</sub> in the reactor, (ii) cool the flue gas stream to saturation in the lower loop, (iii) remove the NO<sub>2</sub> and SO<sub>2</sub> in the 'upper loop' of the absorber, and (iv) remove aerosols using a wet ESP ("WESP").

The apparatus can also be modified to work in conjunction with the '231 process shown collectively as item 202 and comprising a lower loop 206 and WESP 210. A section 204 is added to the process whether it be integral to the '231 process



island 202 as shown in the figure or a stand alone tower with ductwork moving flue gas from one tower to the other. The initial steps of the process are the first steps of the '231 process: (i) cool the flue gas stream to saturation in the lower loop, (ii) remove the SO<sub>2</sub> in the absorber, and (iii) remove aerosols with a WESP.

In order to capture CO<sub>2</sub>, additional mass transfer sections are needed and are collectively shown as the new CO<sub>2</sub> and NH<sub>3</sub> absorption mass transfer section 204. This section will be used to remove CO<sub>2</sub> and NH<sub>3</sub> using ammonium carbonate. The CO<sub>2</sub> removal 212 and NH<sub>3</sub> capture section 214 can either be separated with a liquid redistribution tray to allow the regeneration products to be added prior to the CO<sub>2</sub> mass transfer section or by a separator tray to allow the liquid used to capture ammonia vapor be sent directly to regeneration. The scrubbing solution is a mixture of ammonium carbonate and bicarbonate and preferably has a carbonate concentration between 3 – 25 wt%. The ammonium carbonate/bicarbonate solution enters the top of the NH<sub>3</sub>/CO<sub>2</sub> removal section 'NH<sub>3</sub> lean' or 'CO<sub>2</sub> rich' because it has previously been used to absorb carbon dioxide increasing the bicarbonate/carbonate ratio and decreasing the pH. Due to the increase in bicarbonate and lower pH, this solution will be able to absorb NH<sub>3</sub> according to the following reaction:



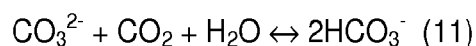
Once the NH<sub>3</sub> has been absorbed, the solution will be captured in a liquid redistribution tray and NH<sub>3</sub>/H<sub>2</sub>O will be added from a regeneration step, which is not a part of this specification. The addition of the NH<sub>3</sub>/H<sub>2</sub>O will further decrease the bicarbonate/ carbonate ratio (meaning the solution is 'NH<sub>3</sub> rich' or 'CO<sub>2</sub> lean') and will be able to absorb CO<sub>2</sub> from the flue gas stream.

## Embodiment 2

### Absorber

Another preferred embodiment is a process for removing CO<sub>2</sub> from a gas stream by scrubbing the CO<sub>2</sub> from the gas stream with a mixture of ammonium and other alkali carbonate compounds such as sodium carbonate and/or potassium carbonate.

The Absorption/Regeneration Equation that is operative in this process is:

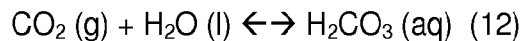


In the absorption process, CO<sub>2</sub> gas and water vapor are absorbed into a carbonate solution forming bicarbonate. It is expected that the hydration of CO<sub>2</sub> is the rate-

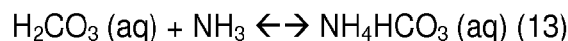
limiting step of the process. Both hydroxide and ammonia increase the rate of hydration of CO<sub>2</sub>. However, increasing the pH of the solution to a regime where hydroxide is present for CO<sub>2</sub> scrubbing would require a large addition of base such as NaOH or KOH. Operating an ammonium carbonate solution under conditions where the CO<sub>2</sub> hydration is fast and the capacity of CO<sub>2</sub> is large enough to be economical brings the process into a regime where the ammonia vapor pressure is large and difficult to manage. Therefore, a mixture of ammonia with another alkali such as potassium or sodium is used to maximize the absorption capacity of the solution for CO<sub>2</sub>, maintain the high rate of CO<sub>2</sub> hydration during the scrubbing process, and minimize the ammonia volatility and release from the absorption process.

The process of the present invention, like the '263 process, uses ammonia in the absorber section. Instead of absorbing SO<sub>2</sub>, the present invention process uses the ammonia to help absorb carbon dioxide (CO<sub>2</sub>) from power plant flue gas. For the present invention process to work properly, most of the SO<sub>2</sub> must be removed from the flue gas before it enters the present invention process.

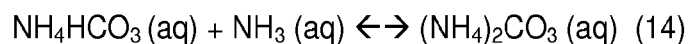
The source of the ammonia for the present invention process is aqua ammonia (NH<sub>4</sub>OH). The carbon dioxide in the flue gas dissolves into the absorber water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>) as shown in Reaction 12.



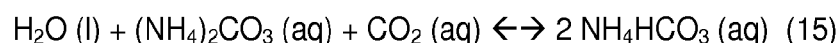
Some of the CO<sub>2</sub> reacts with the NH<sub>3</sub> from to form ammonium bicarbonate (HCO<sub>3</sub><sup>-</sup>) as shown in Reaction 13.



The bicarbonate can further react with more NH<sub>3</sub> to form ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) as shown in Reaction 14.

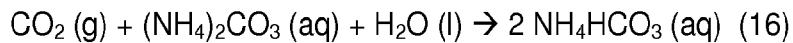


For the CO<sub>2</sub> absorption in the present invention process, the carbonate from Reaction 14 reacts with the carbon dioxide in Reaction 12 to form two bicarbonate ions as shown in Reaction 15.

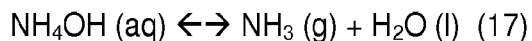


During the regeneration reaction, the HCO<sub>3</sub><sup>-</sup> is converted back to the carbonate CO<sub>3</sub><sup>2-</sup> form as the captured CO<sub>2</sub> is released (see regenerator Reaction 18).

The net absorption reaction from combining Reactions 12 and 15 is shown below.



One undesirable side reaction is the release of some ammonia from the present invention absorber solution. Reaction 17 is the reverse of the Reaction 3. Aqueous ammonia in the absorber liquid enters the flue gas as gaseous ammonia ( $\text{NH}_3$ ). This lost ammonia is referred to as ammonia "slip" and most of this ammonia is recaptured at the top of the present invention absorber and converted to ammonium sulfate. (See capture Reactions 23 through 26.)



### **Maintaining Proper Water Balance in the Absorber**

Depending on the inlet and outlet temperatures to and from the absorber of the present invention, there may be a net change in the amount of water leaving with the treated flue gas. If the inlet flue gas to the absorber is saturated and at a higher temperature than the absorber, water vapor in the flue gas may condense in the absorber. Likewise, if the inlet flue gas is not saturated or is at a significantly lower temperature than the absorber temperature, net evaporation occurs and water is lost from the absorber carbonate solution to the outlet flue gas.

There is a significant benefit to operating the absorber of the present invention under conditions where there is a net loss or no loss of water from the absorber liquid to the flue gas. Under these conditions, water is continually added to the absorber and the purge rate from the absorber is controlled to limit the buildup of inert substances in the carbonate solution. If a significant amount of water condenses out of the flue gas into the carbonate solution in the absorber (more than the purge required for inert removal), the purge rate may be controlled by the increase in water in the system and would require a higher purge rate to control water buildup. This higher purge rate results in higher losses of carbonate counter-ion and other additives that may be in the absorber solution.

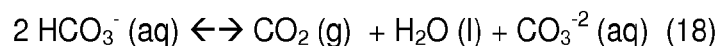
Turning to Fig. 2, one means to prevent excess water accumulation in the carbonate solution is to cool the flue gas from the '231 process 120 with a gas cooler 115 before it enters the absorber 116. The '231 process and equipment 120 also includes an oxidation means that could be a dielectric barrier discharge reactor 107, an ammonia-based scrubbing solution 109, a wet electrostatic precipitator 111, and upper loop 112. Additional apparatus includes a reagent makeup 114 and ammonia capture tank 118. Fig. 7 shows the method, in which the cooling step would be

between the '231 process 250 and CO<sub>2</sub> scrubbing process 252. As the flue gas is cooled, some water vapor in the flue gas may condense out of the flue gas. This condensed water can be used as the makeup water to the process or for other applications at the power plant. The primary purpose, and benefit, of cooling the inlet flue gas is to control the water balance in the absorber itself to reduce the purge rate from the process of the present invention. It also reduces the required size of the gas cooler, which saves capital expense, and is an example of the synergy between the '231 process and the process of the present invention. Instead of using a gas cooler 115, others have cooled liquid water, which misses the benefits of the water balance according to the present invention.

Once the absorption solution is saturated with CO<sub>2</sub> it must be regenerated. The solution is regenerated by heating the solution to release CO<sub>2</sub> as shown as the reverse of Reaction 11.

### Regenerator

The liquid leaving the bottom of the absorber contains the absorbed CO<sub>2</sub> in the form of bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) plus the ammonium from the aqueous ammonia. During regeneration, Reaction 15 is reversed as shown below.



The carbonate ion (CO<sub>3</sub><sup>2-</sup>) consumed during absorption Reaction 15 is recovered in Reaction 18.

The regeneration energy is very important to the economics of the process. Evaluation of the reaction energies suggests the energy consumption for Reaction 11 is the same whether Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> is used. However, to operate the Na<sup>+</sup> or K<sup>+</sup> system in a regime for fast CO<sub>2</sub> absorption would also require the regeneration of the base. Since both NaOH and KOH are strong bases, the energy consumption for recovery is likely to limit the applicability for the Na<sup>+</sup> and K<sup>+</sup> analogs. The  $\Delta H_{\text{rxn}} = -44.5$  and  $-57.5$  kJ/mol for the dissolution of NaOH and KOH respectively. However, with NH<sub>3</sub> present in solution, the high rate of CO<sub>2</sub> hydration is still available and since NH<sub>3</sub> is a weak base the dissolution energy is 5 kJ/mol allowing regeneration of ammonia in the mixed alkali solution to be economically feasible in the process.

The following is a detailed description of the regenerator of the present invention. CO<sub>2</sub> is removed from the flue gas of coal-fired power plants through absorption into a carbonate solution. Due to the mass flow of CO<sub>2</sub> in the flue gas,

economics require that the process provide a way to release the CO<sub>2</sub> and reuse the carbonate solution. For the present invention, a thermal swing absorption process is used.

Figure 8A shows a drawing of the regenerator system. The regenerator consists of the following major pieces of equipment: (i) regenerator tower 502, (ii) feed pump 504, (iii) re-boiler 506, (iv) re-cycle pump 508, cross heat exchanger 516 and (v) lean cooler 510.

**Regenerator Tower** – The regenerator tower 502 is the mass transfer device that allows the CO<sub>2</sub> vapor to be released. Rich CO<sub>2</sub> liquid is fed into the top of the tower through stream 512. This rich liquid comes from the absorption tower after CO<sub>2</sub> has been absorbed from the flue gas stream. As the liquid travels down the regenerator tower it interacts with the vapor rising up the column, and condenses water vapor and releases CO<sub>2</sub> converting bicarbonate to carbonate in the solution. It uses at least one packing section 505. At the same time the concentration of CO<sub>2</sub> in the gas stream increases and the concentration of water vapor decreases. The pH and temperature of the feed solution increases as it goes down the column due to the release of CO<sub>2</sub> and shift from bicarbonate to carbonate. Once in the tower reservoir, the solution is regenerated and is pumped either back to the absorber or to the reboiler 506.

The conditions the regenerator tower operates at will dictate the composition of the CO<sub>2</sub> leaving the regenerator. The pressure of the tower is dictated by the temperature of the liquid leaving the regenerator (stream 514) while the composition of the gas out of the regenerator is dictated by the equilibrium conditions of the feed liquid entering the regenerator (stream 512). The temperature profile down the tower increases from top to bottom, with the highest temperature at the bottom. The pH of the solution increases from top to bottom, with the highest pH solution at the bottom. The composition of the liquid, the total carbonate concentration, decreases from top to bottom with the lowest total carbonate concentration at the bottom.

**Re-boiler** – Integral to the regenerator is a heat exchanger that we have been calling a “reboiler” 506. The term is common in distillation and stripping operations but one actually does not boil the liquid within the device. But like a reboiler it is the means to put energy into the system, causing regeneration of the scrubbing solution. The

total energy supplied by the reboiler 506 is to meet the needs for regeneration, which consist of 1) the heat of reaction to liberate CO<sub>2</sub> from the bicarbonate solution, 2) the sensible heat change required to get the reaction to proceed at a commercially practical rate and 3) the energy for of vaporizing water and ammonia, which is to be minimized but also occurs. The reboiler 506 is fed with a portion of the liquid leaving the regenerator tower. In the reboiler the liquid is heated to an elevated temperature, but kept under pressure so that no boiling occurs. The heated solution is then sprayed into the bottom of the regenerator, at which point a portion of the liquid evaporates (or flashes). The temperature of the reboiler outlet liquid established the regenerator pressure, which is used to maximize the CO<sub>2</sub> content of the regenerator outlet gas. By heating only a portion of the regenerator outlet liquid and returning it to the reboiler one is able to keep the bulk temperature of the regenerator low while maintaining a higher pressure than the bulk temperature would allow. This increases the CO<sub>2</sub> content of the regenerator outlet gas, reducing the total energy input required of the process.

**Cross Heat Exchanger** – The amount of steam the process consumes can be dramatically reduced with heat integration. The method of heat integration in this invention is the use of a cross heat exchanger 516 in which hot lean solution (stream 518) preheats the rich cool solution (stream 520) before entering the regenerator tower 502 and at the same time cools the lean solution (stream 522) before it is returned to the absorber to be reused. The cross heat exchanger 516 is a plate heat exchanger and is based on design approach temperature of 4 – 6 degrees C. This is required due to the large amount of energy, which needs to be transferred between the rich and lean solutions, and reduces the sensible heat input requirement. The approach temperature of the cross heat exchanger is a critical part of energy management in the process of the present invention.

**Feed Pump/Recycle Pump**– Recycle pump 508 is used to transfer desired amount of rich cold solution from absorber (stream 524) to cross heat exchanger 516. Hot lean solution from regenerator (stream 514) is fed to both the re-boiler 506 and to the cross heat exchanger 516 with feed pump 504.

**Lean Cooler** - Since the cross heat exchanger only provides a 4 – 6 degrees C approach temperature, some cooling of the solution is required prior to reintroducing the liquid to the absorber to achieve the required inlet absorption temperature. The lean cooler 510 uses cooling water to achieve the additional 4 – 6 degrees C of cooling required. The cooling load is an additional cost of the system of the present invention, so again good performance and low approach temperatures are required from the cross heat exchanger 516 to provide reasonable costs for energy in the process.

**Summary** – The regenerator 502 is a critical piece of equipment in the process of the present invention. The design must provide for heat recovery and promote CO<sub>2</sub> to be released with minimum water and ammonia evaporation to be economical.

### **Alternative Regenerator Configurations to Reduce Heating and Cooling Requirements.**

The basic process of this invention uses steam to supply the heat to the carbonate solution using a reboiler 506. The vapors (stream 503) leaving the regenerator 502 contain a mixture of carbon dioxide, ammonia and water vapor. These vapors are cooled to remove some of the water and ammonia before compression. Alternative designs to reduce both heating and cooling requirements include a multi-effect design and a vapor recompression design.

In a multi-effect design, steam (or another heat source) is used to supply heat to one regenerator (Regenerator #1). The heat from condensing the vapors leaving Regenerator #1 could be used as the heat source to another regenerator (Regenerator #2). The vapors from Regenerator #2 could likewise be used to supply heat to yet another regenerator, or cooling water could be used to cool the vapors and recover a portion of the ammonia and water, just as in the basic process of the present invention. Typically the regenerators in a multi-effect design would operate at different pressures to optimize heat transfer. The regenerators may also be different sizes to match the condensation heat from the vapors with the reboiler heat requirements of the subsequent regenerator. The benefit of this design is to decrease the overall heating and/or cooling water requirements for the overall process.

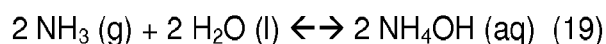
In a vapor recompression design, the vapors leaving the regenerator are compressed and then the heat from condensing the vapors is used as the heat supply to the same regenerator. The compression step is done to increase the temperature at which the vapors condense to allow heat transfer. Some steam may be used to supplement the heat requirements, but the heat in the vapor is used directly to supply heat to the regenerator. Like with the multi-effect design, the overall external heating and cooling requirements are reduced for the process.

In the process of this invention there are significant opportunities for heat recovery and integration. The heat removed from the regenerator vapors and lean liquor may be at high enough temperatures to heat other process streams within the present process or at the attached power plant. Likewise, heat recovery from the compression steps of the present process may also be used within this process or for heating process streams at the attached power plant.

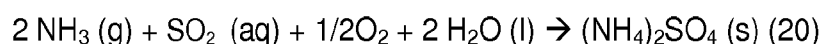
### **Ammonia Capture**

As mentioned previously, some ammonia is released from the absorption section of the present invention process. Since this is a regulated compound, it must be recaptured from the flue gas to reduce ammonia emissions and limit the ammonia make-up requirement. Although the present process regenerator process does not consume ammonia, some is lost to the capture section and that ammonia is converted to ammonium sulfate. A small amount of ammonia (~ 5 ppm) is released from the present invention ammonia capture section into the exiting flue gas.

The first step of the ammonia capture section is to dissolve the ammonia gas (NH<sub>3</sub>) back into the water in the capture solution via Reaction 19. Forming ammonium sulfate requires two molecules of ammonia per ammonium sulfate molecule. Note that Reaction 17 is reversible, so the pH must be low to retain the NH<sub>3</sub> in the liquid and not release it back into the flue gas.



The overall capture reaction is shown in Reaction 20.



The net effect is that the ammonia added to the present invention process is lost from the CO<sub>2</sub> absorption section but reabsorbed in the capture section. When it is reabsorbed, it provides the NH<sub>3</sub> to capture more SO<sub>2</sub>. In other words, the same amount of ammonia is added to the overall system: two molecules of NH<sub>3</sub> for every



molecule of  $\text{SO}_2$ . If the process is running with only '263 process, the ammonia is added to the present invention absorber. If the present invention process is running, some of the ammonia added to the present invention absorber escapes to the capture section and then it is sent back to the '263 process. The ammonia that escapes from the present process is re-used in the '263 scrubber and does not result in a net increase in ammonia consumption. This is an example of a synergy in the system.

Turning to Fig. 9, the scrubbing tower 116 is broken into two sections, 202 and 204, as in the previous embodiment. For more efficient removal of  $\text{CO}_2$ , the  $\text{SO}_2$  and  $\text{NO}_x$  are removed from the flue gas stream 202. The preferred method of  $\text{SO}_2$  and  $\text{NO}_x$  removal is through an ammonia scrubbing solution similar to that described in US Patents 6,605,263 and 6,936,231 where flue gas is cooled to saturation in a lower loop 206 prior to entering a mass transfer section. In the mass transfer section upper loop 208 the  $\text{SO}_2$  and  $\text{NO}_x$  are removed using a pH controlled ammonium sulfate solution. Finally, aerosols or particulates are removed using a device such as a wet electrostatic precipitator 210. Once  $\text{SO}_2$  and  $\text{NO}_x$  are removed from the flue gas stream, the carbon dioxide is captured in the  $\text{CO}_2$  capture section 212.

The solution used in the  $\text{CO}_2$  capture section is a mixture of potassium and ammonium carbonate or sodium and ammonium carbonate 218. The solution goes through the  $\text{CO}_2$  mass transfer section 212, removing  $\text{CO}_2$  from the flue gas stream and producing a carbonate/bicarbonate solution. The mixed alkali bicarbonate solution is then regenerated by heating at an elevated temperature 220 releasing  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ . The  $\text{CO}_2$  is separated from the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  222 and is a substantially pure  $\text{CO}_2$  stream that could be further processed to produce a sequestration-ready  $\text{CO}_2$  stream. The  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are returned to the regenerated potassium carbonate solution and fed back into the scrubber.

Experiments have shown there are acceptable ranges of concentrations and acidity of the carbonate/bicarbonate solution to carry out the process of the present invention. It has been found that an acceptable range of carbonate/bicarbonate concentration is 5 to 20 wt%, ammonium is 0.1 to 3 wt% and alkali is 4 to 25 wt%. The solution would have a pH between 8.5 and 12.

Experiments have also shown optimum ranges of concentrations and acidity of the carbonate/bicarbonate solution. The optimum carbonate/bicarbonate

concentration of 7 to 8 wt%, ammonium of 0.20 to 0.25 wt%, and potassium of 7 to 8 wt%. The optimum pH range is between 10 and 10.5.

Some advantages of using a mixed alkali system include:

1. Lower ammonia vapor pressures for solutions with the same capacity compared to ammonium carbonate solutions
2. Higher rate of CO<sub>2</sub> hydration and therefore requirements for smaller mass transfer devices compared to sodium or potassium carbonate scrubbing solutions.
3. Higher carbonate concentrations for a given pH can be run compared to ammonium carbonate solutions improving the capacity of the solution.

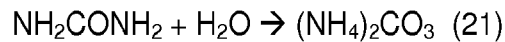
### **Embodiment 3**

This is an optional embodiment of the present invention in which the ammonium carbonate used in the absorber is made onsite from urea. It is a method and apparatus that teaches how a urea solution is hydrolyzed and captured to form an ammonium carbonate solution, as well as how the system is controlled to maintain the performance of an ammonia scrubber. Fig. 10 shows a process 270 according to the present invention. A urea solution 272 is provided in the range of 10 – 60% by weight of urea.

In method 1, the urea is heated in a closed vessel, hydrolyzer 274. As the urea solution is heated the urea decomposes and releases CO<sub>2</sub>, NH<sub>3</sub>, and water vapor. The vapor stream is released from the hydrolyzer vessel and contacted 276 with water in an ammonium carbonate solution tank. The CO<sub>2</sub>, NH<sub>3</sub>, and water vapor condense and react to generate additional ammonium carbonate solution. As the ammonium carbonate solution is removed from the ammonium carbonate tank to be used in a process as ammonia, the pressure control valve on the hydrolyzer opens to release more vapor to replace the ammonium carbonate that was used. Opening the valve decreases the pressure in the hydrolyzer. As the pressure decreases, heat input increases to decompose more urea and generate additional CO<sub>2</sub>, NH<sub>3</sub>, and water vapor. Water is added 278 to the ammonium carbonate tank to maintain the desired concentration by monitoring the specific gravity or conductivity of the. It is desirable to maintain the concentration of ammonium carbonate between 5 and 30

wt% so the minimum amount of water is added 278 to the ammonia scrubbing process.

In method 2, the urea is also hydrolyzed in a urea hydrolyser 274. In this case, as the temperature of the urea solution is increased, the pressure is maintained high enough to inhibit vaporization of the CO<sub>2</sub>, NH<sub>3</sub>, and water vapor. Instead the reaction proceeds in the liquid phase as shown in equation 21.



Completing the reaction in the liquid phase requires substantially less energy since no vaporization is taking place. In addition, this reaction is highly exothermic and therefore the heat generated from the conversion of urea to ammonium carbonate can sustain the decomposition of urea with minimal energy input. The rate of urea conversion in the liquid phase depends on the temperature of operation. Increasing temperature increases the rate of conversion in the range of 38 – 260 degrees C (100 – 500 degrees F). In this method, the initial urea concentration can be chosen to provide the desired ammonium concentration after conversion or to minimize energy, more concentrated urea solutions can be used and water can be added to the product ammonium carbonate to attain the desired ammonium carbonate concentration.

Once the ammonium carbonate solution is generated, it can be used as an ammonia substitute in processes requiring ammonia addition. For example, ammonium carbonate solution is added 280 to a process that removes SO<sub>2</sub> using ammonia. Ammonium carbonate is added to the solution instead of aqueous ammonia to maintain pH as required based on the desired pollutant removal percentage.

Turning to Fig. 11 the sample apparatus 300 of the present invention starts with urea in a hopper 302. The urea is fed by a conveyor 304 to a urea tank 306 where it is maintained at a concentration between 10 % and 60 % by weight.

The urea solution is hydrolyzed in a hydrolyser 308 to create an NH<sub>3</sub>, CO<sub>2</sub>, and water vapor stream (method 1) or an ammonium carbonate solution (method 2). For method 1, the vapor stream is held at elevated temperatures, meaning a temperature above that used in decomposition, until it is brought into contact with water in an ammonium carbonate solution tank 310 to prevent additional reactions from occurring which create solids in the vapor transport line. Water is added to the ammonium carbonate tank to keep the concentration of ammonium carbonate

between 5 % and 30% by weight. Ammonium carbonate solution is then added to an ammonia scrubbing process to maintain pH as required based on a desired percentage of pollution removal.

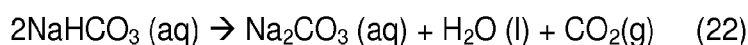
#### Embodiment 4

The next embodiments focus on the regeneration steps. The invention comprises the steps of providing a solution containing  $\text{NH}_4\text{HCO}_3$  /  $(\text{NH}_4)_2\text{CO}_3$  made by carbon dioxide scrubbing; adding  $\text{Na}_2\text{CO}_3$  to precipitate  $\text{NaHCO}_3$  and release  $\text{NH}_3$  vapor; capturing the  $\text{NH}_3$  vapor to make reusable for carbon dioxide scrubbing; and decomposing the  $\text{NaHCO}_3$  with heat greater than 60 degrees C to release carbon dioxide.

Fig. 12 is a flow chart of the process of the present invention. The ammonium carbonate/bicarbonate solution comes from a carbon dioxide scrubbing process and apparatus with ammonium carbonate 320 that results in a solution of  $\text{NH}_4\text{HCO}_3$  /  $(\text{NH}_4)_2\text{CO}_3$ . The solution is transferred to the regeneration system to recover  $\text{NH}_3$  and  $\text{CO}_2$ .

In this approach,  $\text{Na}_2\text{CO}_3$  is added to the  $\text{NH}_4\text{HCO}_3/(\text{NH}_4)_2\text{CO}_3$  solution used in the scrubbing process 320 to precipitate  $\text{NaHCO}_3$  and release  $\text{NH}_3$  vapor in the ammonia release step 322. This can be done at elevated temperature to make the  $\text{NH}_3$  release more efficient. Once released, the  $\text{NH}_3/\text{H}_2\text{O}$  vapor mixture would need to be cooled or condensed or captured by other means such as absorption or adsorption prior to sending back to the carbon dioxide scrubbing process 320 mentioned above.

The  $\text{NaHCO}_3$  slurry can then be heated 326 for decomposition. This step may require that the solid  $\text{NaHCO}_3$  be separated from the  $\text{NH}_4\text{HCO}_3/\text{Na}_2\text{CO}_3$  solution using a filter and rinse to avoid carrying  $\text{NH}_3/\text{NH}_4^+$  to the decomposition reactor/  $\text{CO}_2$  release tank where it could be released with the  $\text{CO}_2$  324. This may also make the decomposition more efficient because one can bring over only the  $\text{NaHCO}_3$  and create a very concentrated solution limiting the amount of water that needs to be heated. The decomposition of  $\text{NaHCO}_3$  occurs at temperatures  $>60$  °C and is described by the following reaction:



The decomposition process 324 recovers the  $\text{Na}_2\text{CO}_3$  required to release the  $\text{NH}_3$  and has been done commercially as part of the Solvay process to create  $\text{Na}_2\text{CO}_3$ .

Again some cooling 328 will be required prior to returning the  $\text{Na}_2\text{CO}_3$  to the  $\text{NH}_3$  recovery due to the need for the  $\text{NH}_3$  recovery and the  $\text{CO}_2$  recovery to operate at different temperatures. The temperature values chosen are based on physical property information. This is an improvement over what others have used in the past to recover  $\text{NaHCO}_3$  for their dry scrubbing steps. The difference is that there is not necessarily a requirement for a purge step that would remove sodium from the process. Since it is not volatile, it will not be carried out in either of the recovery steps, minimizing the need for sodium makeup.

Depending on the amount of ammonium sulfate, nitrate, and chloride compounds captured in a carbon dioxide scrubbing mass transfer section, it may be necessary to purge sulfates, nitrates and chlorides from the ammonium carbonate/bicarbonate solution to the UL or LL of the sulfur dioxide scrubbing mass transfer section. This would cause the  $\text{CO}_2$  to be released back into the scrubber and would also keep the amount of sulfates, nitrates, and chlorides in the ammonium carbonate scrubbing and regenerating loops to a minimum. The size of this stream will depend on the capture efficiency of the upper loop and by the amount of aerosols that are captured in the carbon dioxide scrubbing mass transfer section.

Fig. 13 is a schematic diagram of an apparatus according to the present invention. Ammonium carbonate/bicarbonate solution comes from a carbon dioxide scrubbing process and apparatus 204 with ammonium carbonate that results in a solution of  $\text{NH}_4\text{HCO}_3$  /  $(\text{NH}_4)_2\text{CO}_3$  in a tank 330. The solution is transferred to the regeneration system to recover  $\text{NH}_3$  and  $\text{CO}_2$ .

In this approach,  $\text{Na}_2\text{CO}_3$  is added to the  $\text{NH}_4\text{HCO}_3/(\text{NH}_4)_2\text{CO}_3$  solution 330 used in the scrubbing process to precipitate  $\text{NaHCO}_3$  and release  $\text{NH}_3$  vapor in the  $\text{NH}_3$  release tank 332. This can be done at elevated temperature to make the  $\text{NH}_3$  release more efficient. Once released, the  $\text{NH}_3/\text{H}_2\text{O}$  vapor mixture would need to be cooled, condensed, or captured by other means such as absorption or adsorption 334 prior to sending back to the carbon dioxide scrubbing process.

The  $\text{NaHCO}_3$  slurry can then be heated and sent to a heater 336 for decomposition. This step may require that the solid  $\text{NaHCO}_3$  be separated from the  $\text{NH}_4\text{HCO}_3/\text{Na}_2\text{CO}_3$  solution using a filter and rinse to avoid carrying  $\text{NH}_3/\text{NH}_4^+$  to the decomposition reactor/  $\text{CO}_2$  release tank 340 where it could be released with the  $\text{CO}_2$ . This may also make the decomposition more efficient because one can bring

over only the  $\text{NaHCO}_3$  and create a very concentrated solution limiting the amount of water that needs to be heated.

The decomposition process recovers the  $\text{Na}_2\text{CO}_3$  required to release the  $\text{NH}_3$  and has been done commercially as part of the Solvay process to create  $\text{Na}_2\text{CO}_3$ . Again some cooling with a cooler 338 will be required prior to returning the  $\text{Na}_2\text{CO}_3$  to the  $\text{NH}_3$  recovery due to the need for the  $\text{NH}_3$  recovery and the  $\text{CO}_2$  recovery to operate at different temperatures.

Depending on the amount of ammonium sulfate, nitrate, and chloride compounds captured in the carbon dioxide scrubbing mass transfer section 204, it may be necessary to have a purge stream from the ammonium carbonate/bicarbonate tank 330 to the UL or LL of the carbon dioxide scrubbing mass transfer section 204. This would cause the  $\text{CO}_2$  to be released back into the scrubber and would also keep the amount of sulfates, nitrates, and chlorides in the ammonium carbonate scrubbing and regenerating loops to a minimum. The size of this stream will depend on the capture efficiency of the upper loop and by the amount of aerosols that are captured in the carbon dioxide scrubbing mass transfer section 204.

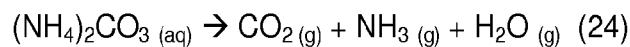
### **Embodiment 5**

This embodiment is a method and apparatus for controlling ammonia and water vapor from a stream created from the decomposition of ammonium carbonate, returns the ammonia and water reagents to other processes for reuse and creates a carbon dioxide stream that is sequestration ready comprising the steps of washing the gas stream mixture containing carbon dioxide, ammonia, and water with a  $\text{CO}_2$  rich carbonate solution; condensing water vapor with a cooling step, drying the remaining gas stream to a dewpoint of less than  $-40$  degrees C ( $-40$  °F), and compressing the purified carbon dioxide stream to sequestration pressures.

Turning to Fig. 14 and Fig. 15 at the same time, flue gas typically contains  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{CO}_2$  342, 362. The  $\text{SO}_2$  and  $\text{NO}_x$  are preferably processed by the method and apparatus disclosed in U.S. Pat. No. 6,991,771, and U.S. Pat. No. 6,936,231. It is referred to in this specification as the '231 System 344, 364. The  $\text{CO}_2$  scrubbing process and apparatus can be integral with the apparatus island of the '771 or the '231 process, or it can be in its own tower with ductwork moving flue gas from one tower to the other and back. Regardless, after either the '771 or '231

process 344, the CO<sub>2</sub> is scrubbed with an ammonium carbonate solution 346 in a scrubbing apparatus 366. The scrubbing produces ammonium bicarbonate, and the scrubbing solution becomes an ammonium carbonate / ammonium bicarbonate solution 348. A portion of the solution is drawn off and sent to a regeneration step 110 to recover ammonia and produce carbon dioxide for sequestration.

In the ammonium carbonate regenerator 370 that performs the regeneration step 350, the ammonium carbonate solution is heated in an ammonium carbonate decomposer 372 to decompose the ammonium carbonate solution to carbon dioxide, ammonia and water vapor 352 via the following reactions:



For the CO<sub>2</sub> to be acceptable for sequestration, the ammonia and water must be removed from the gas stream. One method to remove the ammonia is to use a CO<sub>2</sub> rich solution to wash the gas stream. The CO<sub>2</sub> rich solution is preferably composed of a concentrated carbonate solution used for CO<sub>2</sub> scrubbing prior to the regeneration step and is at a temperature of 38 – 66 degrees C (100 – 150 °F) and atmospheric pressure. The gas stream that is to be washed to remove NH<sub>3</sub> is preferably at a temperature of > 66 degrees C (150 °F) and a pressure of 0.69 – 34 bars (10 – 500 psi).

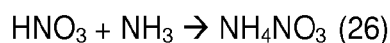
A separate mass transfer section(s) is needed to wash the ammonia laden gas stream, the new NH<sub>3</sub> absorption mass transfer section. This section will be used to remove NH<sub>3</sub> using ammonium carbonate. The NH<sub>3</sub> capture 354, 374 is separated with a liquid redistribution tray but not a separator tray. The scrubbing solution is a mixture of ammonium carbonate and bicarbonate. The concentration of the ammonium carbonate solution is dictated by the CO<sub>2</sub> absorption process but should be as concentrated as possible to improve the efficiency of the regenerator. The ammonium carbonate/bicarbonate solution enters the top of the NH<sub>3</sub> removal section 'NH<sub>3</sub> lean' or 'CO<sub>2</sub> rich' because it has previously been used to absorb carbon dioxide increasing the bicarbonate/carbonate ratio and decreasing the pH. Due to the increase in bicarbonate and lower pH, this solution will be able to absorb NH<sub>3</sub> according to the following reaction:



Once the NH<sub>3</sub> has been absorbed, the carbonate solution continues to the regeneration step. The carbon dioxide stream is now ammonia free and is sent to a heat exchanger 376 to further cool the gas stream to less than 54 degrees C (130 °F). The process of cooling the gas stream causes the water vapor to condense and will also capture any remaining ammonia vapor in the flue gas stream 356. Further or alternative drying of the flue gas can be done using commercially available processes including but not limited to the use of molecular sieves or membranes. The remaining carbon dioxide can be handled by being compressed 358 with a compressor 378.

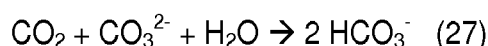
### Embodiment 6

This embodiment is used with the '231 or '771 process and involves scrubbing of ammonia with urea ammonium nitrate solution. As shown in Fig. 16, the ammonium carbonate or mixed alkali solution 402 is circulated to absorb CO<sub>2</sub> from a flue gas stream containing CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub> 404. The solution is sent through a regenerator 406 to produce a concentrated CO<sub>2</sub> stream 408 ready for sequestration. Once regenerated the solution is recycled back to the CO<sub>2</sub> capture section 410 to absorb more CO<sub>2</sub>. In the process of absorbing CO<sub>2</sub> ammonia is released. The amount of ammonia released is determined by the conditions of absorption and the composition of the absorbing solution but will be between 100 – 8000 ppm. After the CO<sub>2</sub> is captured, the flue gas moves to an ammonia capture mass transfer section 412 where a concentrated urea ammonium nitrate solution is circulating. The solution is pH adjusted to between 4 and 6 with nitric acid 414 to make the solution ammonia lean and forms ammonium nitrate as shown in equation (26).



Urea 416 is added to the solution either prior to the NH<sub>3</sub> capture 412 or after the formation of the ammonium nitrate to maintain a concentrated urea ammonium nitrate solution 418 ready for commercial distribution.

As shown in Fig. 17, a flue gas stream containing CO<sub>2</sub> 422 is brought into an absorption section 424 that uses an ammonium carbonate solution to absorb CO<sub>2</sub>. The ammonium carbonate is converted into ammonium bicarbonate 428 through reaction of CO<sub>2</sub> with CO<sub>3</sub><sup>2-</sup> as shown in (27):





The ammonium bicarbonate solution is introduced into the regenerator 430, to reverse reaction (27) creating a concentrated CO<sub>2</sub> stream, which can be processed for sequestration or beneficial use. The regenerated solution is re-introduced into the absorber tower 424 to remove more CO<sub>2</sub>.

Due to the volatility of the ammonium carbonate solution, the flue gas exits the absorber 204 with >70% CO<sub>2</sub> having been removed and with the addition of ammonia vapor. The CO<sub>2</sub> lean flue gas 432 now enters an ammonia vapor recovery 434 section to remove the ammonia vapor prior to leaving the stack. In the ammonia vapor recovery section, nitric acid 436 is added to a urea ammonium nitrate (UAN) solution to decrease the pH to <6. The UAN absorbs the ammonia vapor from the flue gas in a gas liquid contactor. When the UAN exits the contactor, part of the solution is removed as product 438 ready to be used as a fertilizer product while the rest is recycled back to the ammonia vapor recovery section 434. Additional urea 440 and HNO<sub>3</sub> acid 436 are added to maintain the required ratios of UAN and to maintain the ability to absorb NH<sub>3</sub> vapor.

The advantages of using UAN to do ammonia absorption as part of a CO<sub>2</sub> scrubbing process are:

1. The ability to produce a nitrogen fertilizer, which is the predominant plant nutrient required by crops.
2. The ability to produce a nitrogen fertilizer with minimal capital cost. Since the ammonia capture is required in the CO<sub>2</sub> scrubbing process, only incremental increases are required for the nitrogen fertilizer production including pumps and storage allowing one to take advantage of the infrastructure already in place.

### **Embodiment 7**

This is another optional embodiment related to using Raman spectroscopy to control carbonate / bicarbonate concentrations. The invention is a method of controlling carbonate/bicarbonate concentrations in a chemical process having the steps of a) flowing a carbonate/bicarbonate solution through a measurement cell, (b) exposing the solution to laser light of suitable wavelength and power ; c) measuring the intensity of the scattered light using Raman spectroscopy; and d) calculating the concentration of carbonate and bicarbonate from the intensity of the scattered light and (e) sending the measurement results to a programmable logic controller (PLC)

to be used to control the ratio and concentration of carbonate and bicarbonate in the solution through adjusting process parameters.

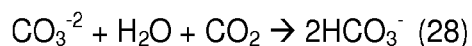
Raman spectroscopy depends upon the inelastic scattering of monochromatic light. The incident light usually comes from a laser in the visible or ultraviolet range. When carbonate and/or bicarbonate are irradiated with the laser light, they shift the frequency of the light. This shift can be measured for both carbonate and bicarbonate and occurs at different frequencies. Turning to Fig. 18, bicarbonate has a peak 452 at approximately  $1015\text{ cm}^{-1}$  and carbonate has a peak 454 at approximately  $1065\text{ cm}^{-1}$ .

By measuring the intensity of the scattered light either by peak height or peak area, the concentrations of each component can be determined. These two concentrations can then be used to calculate total carbonate.

The invention involves using Raman spectroscopy to identify and quantify carbonate and bicarbonate real time in a process that relies on the ratio of carbonate, and bicarbonate present as well as the total carbonate concentration. To our knowledge, there are presently no alternatives to performing this online.

One embodiment is a carbon dioxide scrubbing process where carbonate and bicarbonate are the main components as shown in Fig. 19.

A "carbonate lean" solution 456 is introduced to a  $\text{CO}_2$  absorption process 458. A carbonate lean solution contains a ratio of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  less than 1. Its composition is measured by a first Raman spectrometer 468. As  $\text{CO}_2$  is absorbed into the carbonate solution, the following general reaction will take place:



As this occurs, the total carbonate and carbonate/bicarbonate ratio will change. A "carbonate rich" solution with  $\text{HCO}_3^-/\text{CO}_3^{2-}$  ratio greater than 1 will exit the absorption process 464. Its composition is measured by a second Raman spectrometer 470. The carbonate/bicarbonate solution can be but is not limited to  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3/\text{NH}_4\text{HCO}_3$ , and  $\text{K}_2\text{CO}_3/\text{KHCO}_3$ . The important factor for controlling the ratio of carbonate and bicarbonate in the solution is that the carbonate be soluble in the solution being measured.

The Raman spectrometers steps 468 and 470 operate more precisely in the following manner as shown in Figure 20. The method comprises the steps of flowing a carbonate/bicarbonate solution through a measurement cell, exposing a carbonate /bicarbonate solution with laser light of suitable wavelength and power ;

measuring the intensity of the scattered light using Raman spectroscopy; calculating the concentration of carbonate and bicarbonate from the intensity of the scattered light, and sending the measurement results to a PLC to be used to control the ratio of carbonate to bicarbonate, and total carbonate in the solution

This method would be used to control the total carbonate concentration and to control the ratio carbonate concentration to bicarbonate concentration. The concentration values would be sent to a ("PLC") 466 as feedback to the process control loops to the process 458. These factors are important because if the carbonate to bicarbonate ratio is not controlled it would lead to poor absorption efficiency. If the total carbonate concentration is not controlled, it would lead to "salting out" or precipitation of the carbonate solution fouling mass and heat transfer surfaces. The method provides feedback to the PLC for adjusting parameters such as, but not limited to liquid flow rates, reagent addition rates, and temperatures.

Turning to Fig. 20, another embodiment and process in which this invention can be used is the production of carbon dioxide from alkali carbonate / bicarbonate solutions. This can also be characterized as a carbonate / bicarbonate regeneration process 476. To produce CO<sub>2</sub> from alkali carbonate / bicarbonate solutions such as, but not limited to Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/NH<sub>4</sub>HCO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub>, the reaction of equation (25) above is reversed. Bicarbonate is converted to carbonate, water and CO<sub>2</sub>.

In such a process, feedback will be necessary to determine if the solution has been regenerated 476 to the degree required to by the process. A method of doing this is to measure the carbonate and bicarbonate concentrations along different points of the process.

A rich HCO<sub>3</sub><sup>-</sup> / CO<sub>3</sub><sup>-2</sup> solution, that is bicarbonate to carbonate ratio greater than 1, 474 is introduced to a regeneration process 476. Its composition is measured by a first Raman spectrometer 480. CO<sub>2</sub> gas 484 is produced as a result of the regeneration process 476. A lean HCO<sub>3</sub><sup>-</sup> / CO<sub>3</sub><sup>-2</sup> solution, that is bicarbonate to carbonate ratio less than 1, 472 exits the regeneration process. Its composition is measured by a second Raman spectrometer 478.

Information from the first and second Raman spectrometers 480, 478 would be fed to a PLC 482, which would then control an energy input to the regeneration process 476. The Raman spectrometers would provide real time data input to a PLC

or other automated controller that could then be used for either regeneration 476 or absorber 458 control.

One embodiment of a measurement system could include, but not be limited to, the following:

- Sample probe;
- Data transfer cables from probe to spectrometer;
- Spectrometer;
- Computer; and
- Output to PLC (analog or digital).

### **Embodiment 8**

This is an embodiment describing clean up of the product gas. In the present process, CO<sub>2</sub> is removed from the flue gas of coal-fired power plants through absorption into a carbonate solution. Due to the mass flow of CO<sub>2</sub> in the flue gas, economics require that the process provide a way to release the CO<sub>2</sub> and reuse the carbonate solution. For the present invention a thermal swing absorption process is used. During the regeneration process, carbon dioxide along with ammonia and water vapor are released. The ammonia and water vapor must be removed prior to sequestration of the CO<sub>2</sub>.

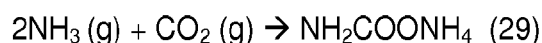
Figure 21 shows a process flow diagram ("PFD") of the CO<sub>2</sub> product gas cleanup process. The CO<sub>2</sub> product gas cleanup process consists of (i) regen condenser 530, (ii) compressor 532, (iii) product condenser 534, and (iv) molecular sieve (or other standard drying system) 536.

The goal of the CO<sub>2</sub> product gas cleanup process is to remove H<sub>2</sub>O and NH<sub>3</sub> from the CO<sub>2</sub> gas stream to make it sequestration-ready. Sequestration ready is best defined by the Kinder Morgan standards. The Kinder Morgan company has set the following specifications for pipeline CO<sub>2</sub>

- a. Product - Substance containing at least ninety five mole percent (95%) of Carbon Dioxide.
- b. Water - Product shall contain no free water, and shall not contain more than 13.6 kg (30 pounds) of water per mmscf in the vapor phase. The specification for vapor phase water of 13.6 kg (30 lbm) per mmscf is equivalent to 264 ppmw using an average molecular weight of 43.2 (based on 95 mol% CO<sub>2</sub> and 5% N<sub>2</sub>).

- c. Hydrogen Sulfide - Product shall not contain more than twenty (20 ppmw) parts per million, by weight, of hydrogen sulfide.
- d. Total Sulfur - Product shall not contain more than thirty five (35 ppmw) parts per million, by weight, of total sulfur.
- e. Temperature - Product shall not exceed a temperature of 49 degrees C (120degrees F).
- f. Nitrogen - Product shall not contain more than four mole percent (4%) of Nitrogen.
- g. Hydrocarbons - Product shall not contain more than five mole percent (5%) of hydrocarbons and the dew point of product (with respect to such hydrocarbons) shall not exceed -29 degrees C (-20 degrees F).
- h. Oxygen - Product shall not contain more than ten (10) parts per million, by weight, of Oxygen.
- i. Other - Product shall not contain more than 1.14 liters (0.3 gallons) of glycol per mmcf and at no time shall such glycol be present in a liquid state at the pressure and temperature conditions of the pipeline.

To meet these requirements, a product gas cleanup process has been developed. Leaving the regenerator tower, the gas stream could contain up to 50% H<sub>2</sub>O vapor. The consequence of this is that the cost to compress the gas stream will be substantially higher than if the gas stream contained less water vapor. Therefore, the initial step is to condense a substantial portion of the water from the gas stream. Condensation is an inexpensive way to achieve the lower water vapor concentration. The conditions in the regenerator condenser 530 are set to achieve <10% H<sub>2</sub>O in the gas stream. In the condensation step, it is important to maintain a minimum water vapor concentration >0.5%. The minimum water vapor concentration is determined by the amount of ammonia remaining in the gas stream after the regen condenser 530. The requirement for a minimum amount of water vapor is due to the following reaction:



where ammonia and carbon dioxide react in the absence of water to form solid ammonium carbamate. When setting the conditions of the first condenser, the goal is to remove as much water as possible without creating conditions that form ammonium carbamate in the condenser or downstream equipment. The carbamate reaction is favored at low water and high ammonia concentrations and is a function of the amount of water vapor and ammonia vapor that are left in the gas stream after the initial condensation step.

After the regen condenser 530, the gas stream is compressed. There are two benefits, (i) pipeline CO<sub>2</sub> pressure will require the pure CO<sub>2</sub> gas stream to be at >69 bars (1000 psi) and (ii) the increased pressure will make the second condensation step more effective at removing H<sub>2</sub>O and the remaining NH<sub>3</sub> vapor prior to the molecular sieves. The compression step will take the gas stream pressure to between 10.3 – 28 bars (150 – 400 psia).

In the second condensation step, the conditions are set to achieve H<sub>2</sub>O and NH<sub>3</sub> concentrations that are acceptable going into the molecular sieve 536. The goal is to remove as much H<sub>2</sub>O and NH<sub>3</sub> as possible with the cooling water available. Adding chillers would improve the capability to remove both H<sub>2</sub>O and NH<sub>3</sub> but the increased cost would need to be evaluated to determine if the incremental improvement in removal was worth the additional cost.

In all of this, the focus has been on only H<sub>2</sub>O and NH<sub>3</sub> removal. However, in each condensation step where cold dilute aqueous ammonia is formed, CO<sub>2</sub> is also absorbed creating an ammonium bicarbonate solution. Therefore, in setting conditions for condensation to occur, care must be taken to minimize CO<sub>2</sub> reabsorption as this creates a CO<sub>2</sub> recycle loop, which is returned to the regenerator to be reheated.

Fig. 22 is a complete process flow diagram ("PFD") for one embodiment of the entire process of the present invention. The parts are described in detail earlier in this specification.

Shown in Table 4 is experimental data on the removal of water and ammonia vapor from the regenerator gas outlet stream. The table provides the gas composition after cooling at the regenerator gas outlet pressure (first stage) and the pressure following gas compression (second stage).

Table 4: Two Stage Condensation and Compression for H<sub>2</sub>O and NH<sub>3</sub> Removal

System	Pressure (psia)	Temperature (F)	First Stage	Second Stage
			28.7	130
Gas In	CO <sub>2</sub>	(%)	30	86.9
	NH <sub>3</sub>	(%)	3.1	0.9
	H <sub>2</sub> O	(%)	66.2	12.2
Gas Out	CO <sub>2</sub>	(%)	87.7	99.7
	NH <sub>3</sub>	(%)	0.9	0.018
	H <sub>2</sub> O	(%)	11.4	0.24

Although the preferred embodiments of the present invention have been described herein, the above description is merely illustrative. Further modification of the invention herein disclosed will occur to those skilled in the respective arts and all such modifications are deemed to be within the scope of the invention as defined by the appended claims.

## Claims

What is claimed is:

1. An apparatus for removing CO<sub>2</sub> from a gas stream comprising:
  - a. a regenerable carbonate scrubbing solution (402) for CO<sub>2</sub> scrubbing comprising a mixture of alkali carbonates;
  - b. an absorption tower (102) adapted to create contact between the flue gas and the scrubbing solution and which operates at a temperature between 32 and 66 degrees C and comprising mass transfer means and liquid distribution means to provide the gas and liquid contact;
  - c. a regeneration tower (502) to release CO<sub>2</sub> from the scrubbing (402) solution, the regeneration tower comprising:
    - i. packing for mass transfer (505);
    - ii. means for allowing the spent scrubbing solution to be introduced at elevated temperature; and
    - iii. means for introducing heat to the regenerator tower (506);
  - d. a controller for controlling the absorption and regeneration system parameters selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and
  - e. a heat recovery device (516) to recover energy during the heating and cooling of the absorption and regeneration column liquids.
2. The apparatus of claim 1, the scrubbing solution comprising sodium, potassium and/or ammonium carbonate, wherein the concentration of carbonate is 0 – 20 wt% and the pH of the solution is 8 – 12.
3. An apparatus for synergistically removing CO<sub>2</sub>, SO<sub>2</sub>, Hg, and particulate matter from a gas stream comprising:
  - an ammonia based scrubbing solution (109) for SO<sub>2</sub> scrubbing;



an SO<sub>2</sub> absorption section (112) to create contact between the flue gas and the ammonia based scrubbing solution to remove SO<sub>2</sub> from the flue gas;

a wet electrostatic precipitator (111) to remove aerosols and fine particulate matter from the flue gas;

a regenerable carbonate scrubbing solution (402) for CO<sub>2</sub> scrubbing comprising a mixture of alkali carbonates;

a CO<sub>2</sub> absorption section (110) for removal of CO<sub>2</sub> adapted to create contact between the flue gas and the scrubbing solution and which operates at a temperature between 32 and 66 degrees C and comprising mass transfer means and liquid distribution means to provide the gas and liquid contact;

an ammonia absorption section (108) to capture ammonia vapor which creates contact between at least some of the liquid leaving the SO<sub>2</sub> absorption section and the gas leaving the CO<sub>2</sub> absorption section and return ammonia rich liquid leaving the CO<sub>2</sub> absorption section to the SO<sub>2</sub> absorption section for use in SO<sub>2</sub> capture;

a regeneration tower (502) to release CO<sub>2</sub> from the scrubbing solution (402), the regeneration tower comprising:

packing for mass transfer;

means for allowing the spent scrubbing solution to be introduced at elevated temperature; and

means for introducing heat to the regenerator tower (506);

a controller for controlling the absorption and regeneration system parameters selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and

a heat recovery device (516) to recover energy during the heating and cooling of the absorption and regeneration column liquids.

4. The apparatus of claim 3, the scrubbing solution comprising sodium, potassium and/or ammonium carbonate, wherein the concentration of carbonate is 0 – 20 wt% and the pH of the solution is 8 – 12.
5. The apparatus of claim 3, the ammonia capture section comprising a mass transfer to create contact between the flue gas and scrubbing solution to remove ammonia vapor that is released during CO<sub>2</sub> scrubbing.
6. The apparatus of claim 3, the ammonia capture solution comprising an ammonia based scrubbing solution used for the SO<sub>2</sub> scrubber.
7. The apparatus of claim 3 where the WESP is replaced with a bag house or fabric filter.
8. The apparatus of claim 3 further comprising a gas cooler (115) for condensing water vapor from the gas stream before the CO<sub>2</sub> absorption section (110).
9. An apparatus for synergistically removing CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, Hg, and particulate matter from a gas stream comprising:
  - an ammonia based scrubbing solution (109) for SO<sub>2</sub> and NO<sub>x</sub> scrubbing;
  - a means of oxidation to convert NO to NO<sub>2</sub> and HNO<sub>3</sub>;
  - an SO<sub>2</sub> / NO<sub>2</sub> absorption tower to create contact between the flue gas and the ammonia based scrubbing solution to remove SO<sub>2</sub> and NO<sub>2</sub> from the flue gas;
  - a wet electrostatic precipitator (111) to remove aerosols and fine particulate matter from the flue gas;
  - a regenerable carbonate scrubbing solution (402) for CO<sub>2</sub> scrubbing containing a mixture of alkali carbonates;
  - a CO<sub>2</sub> absorption section (110) to create contact between the flue gas and the scrubbing solution, which operates at a temperature between 32 and

66 degrees C and comprising a mass transfer means and liquid distribution means to provide the gas and liquid contact;

an ammonia absorption section (108) to capture ammonia vapor which creates contact between all or a portion of the liquid leaving the first absorption section and the gas leaving the CO<sub>2</sub> absorption section and return ammonia rich liquid leaving the CO<sub>2</sub> absorption section to the SO<sub>2</sub> / NO<sub>2</sub> absorption section for use in SO<sub>2</sub> capture;

a regeneration section 502 to release CO<sub>2</sub> from the scrubbing solution, the regeneration tower comprising:

packing for mass transfer;

means for allowing the spent scrubbing solution to be introduced at elevated temperature; and

means for introducing heat to the regenerator tower;

a controller for controlling the absorption and regeneration system parameters selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and

a heat recovery device to recover energy during the heating and cooling of the absorption and regeneration column liquids.

10. The apparatus of claim 9 the scrubbing solution comprising sodium, potassium and/or ammonium carbonate, wherein the concentration of carbonate is 0 – 20 wt% and the pH of the solution is 8 – 12.

11. The apparatus of claim 9 wherein the WESP is replaced with a bag house or fabric filter.

12. The apparatus of claim 9 where the oxidation means is a dielectric barrier discharge reactor.

13. The apparatus of claim 12 where an additive comprising propene or H<sub>2</sub>O<sub>2</sub> is used to improve oxidation efficiency of the dielectric discharge reactor.
14. A process for removing CO<sub>2</sub> from a gas stream comprising the steps of:
- absorbing CO<sub>2</sub> with a carbonate solution between 32 and 66 degrees C;
  - regenerate the carbonate solution by heating and releasing CO<sub>2</sub>;
  - controlling the absorbing and regenerating steps using inputs selected from the group consisting of gas inlet temperature, reagent feed rates, regeneration temperature and pressure, and system differential pressure; and
  - providing a heat recovery device.
15. The process of claim 14 wherein the carbonate solution comprises alkali carbonates, the carbonate solution concentration is between 0 and 20 wt % and the pH of the carbonate solution is between 8 and 12.
16. A method for producing a CO<sub>2</sub> stream from the decomposition of ammonium carbonate comprising the steps of:
- washing a gas stream containing CO<sub>2</sub>, ammonia, and water with a CO<sub>2</sub>-rich carbonate solution (354); followed by
  - condensing at least some of the water from the gas stream by cooling (356); followed by
  - drying the gas stream so that it has a dewpoint of -40 degrees C thereby removing substantially all of the water; and
  - compressing the remaining gas.
17. The method of claim 16, wherein the CO<sub>2</sub>-rich carbonate solution is between 38 degrees C and 66 degrees C.
18. The method of claim 16, wherein the cooling cools the gas stream to less than 54 degrees C.

19. The method of claim 16, further comprising the step of scrubbing CO<sub>2</sub> with an ammonium carbonate solution (346) before the washing step (354).

20. A method of controlling carbonate/bicarbonate concentrations in a chemical process comprising the steps of:

flowing a carbonate/bicarbonate solution through a measurement cell;  
exposing the solution to laser light of suitable wavelength and power;  
measuring the intensity of the scattered light using Raman spectroscopy;  
calculating the concentration of carbonate and bicarbonate from the

intensity of the scattered light; and

sending the measurement results to a programmable logic controller (466)

to be used to control the ratio of carbonate to bicarbonate and total carbonate concentration in the solution through adjusting process parameters.

21. A method of controlling bicarbonate/carbonate concentrations in a CO<sub>2</sub> absorption process comprising the steps of:

providing a lean bicarbonate/carbonate solution having a bicarbonate/carbonate ratio of less than 1 (456);

measuring the lean bicarbonate/carbonate composition with a first Raman spectrometer (468);

absorbing CO<sub>2</sub> (458) with a bicarbonate/carbonate solution, thereby producing a rich bicarbonate/carbonate solution having a bicarbonate/carbonate ratio greater than 1 (464);

measuring the rich bicarbonate/carbonate solution with a second Raman spectrometer (470); and

sending the lean bicarbonate/carbonate composition measurement and rich bicarbonate/carbonate to a programmable logic controller (466) for controlling the CO<sub>2</sub> absorption process (458).

22. A method of controlling alkali bicarbonate/carbonate solutions in a bicarbonate/carbonate regeneration process comprising the steps of:

providing a rich bicarbonate/carbonate solution having a bicarbonate/carbonate ratio greater than 1 (474);

measuring the rich bicarbonate/carbonate solution with a first Raman spectrometer (480);  
regenerating the bicarbonate/carbonate solution (476) thereby producing CO<sub>2</sub> (484) and a lean bicarbonate/carbonate solution having a bicarbonate/carbonate ratio of less than 1 (472);  
measuring the lean bicarbonate/carbonate solution with a second Raman spectrometer (478); and  
sending the rich bicarbonate/carbonate composition measurement and lean bicarbonate/carbonate to a programmable logic controller (482) for controlling the regeneration process (476).

23. A method of treating a CO<sub>2</sub> removal product gas stream gas stream comprising CO<sub>2</sub> ammonia, and water vapor comprising the steps of:

condensing the gas stream with a regenerator condenser by chilling so that there is between 0.5 %and 10% water by weight in the gas stream (530); followed by  
compressing the gas stream with a product compressor to a pressure between 10.3 and 27.6 bar (532); followed by  
condensing the gas stream with a product condensor by chilling while maintaining greater than 0.5% water by weight in the gas stream; followed by  
removing water and ammonia from the gas stream with a molecular sieve (536).

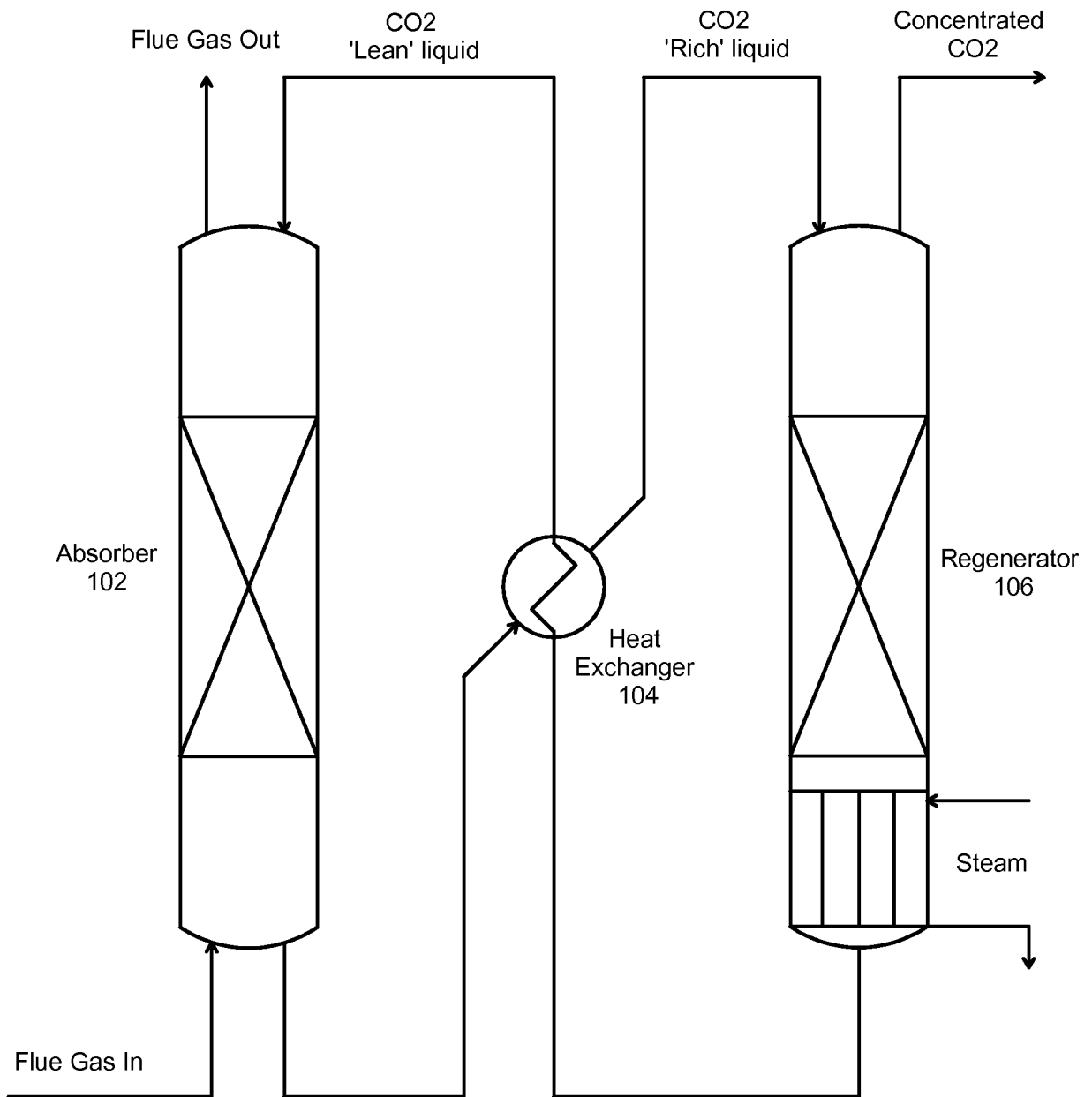


Fig. 1. Basic thermal swing absorption process

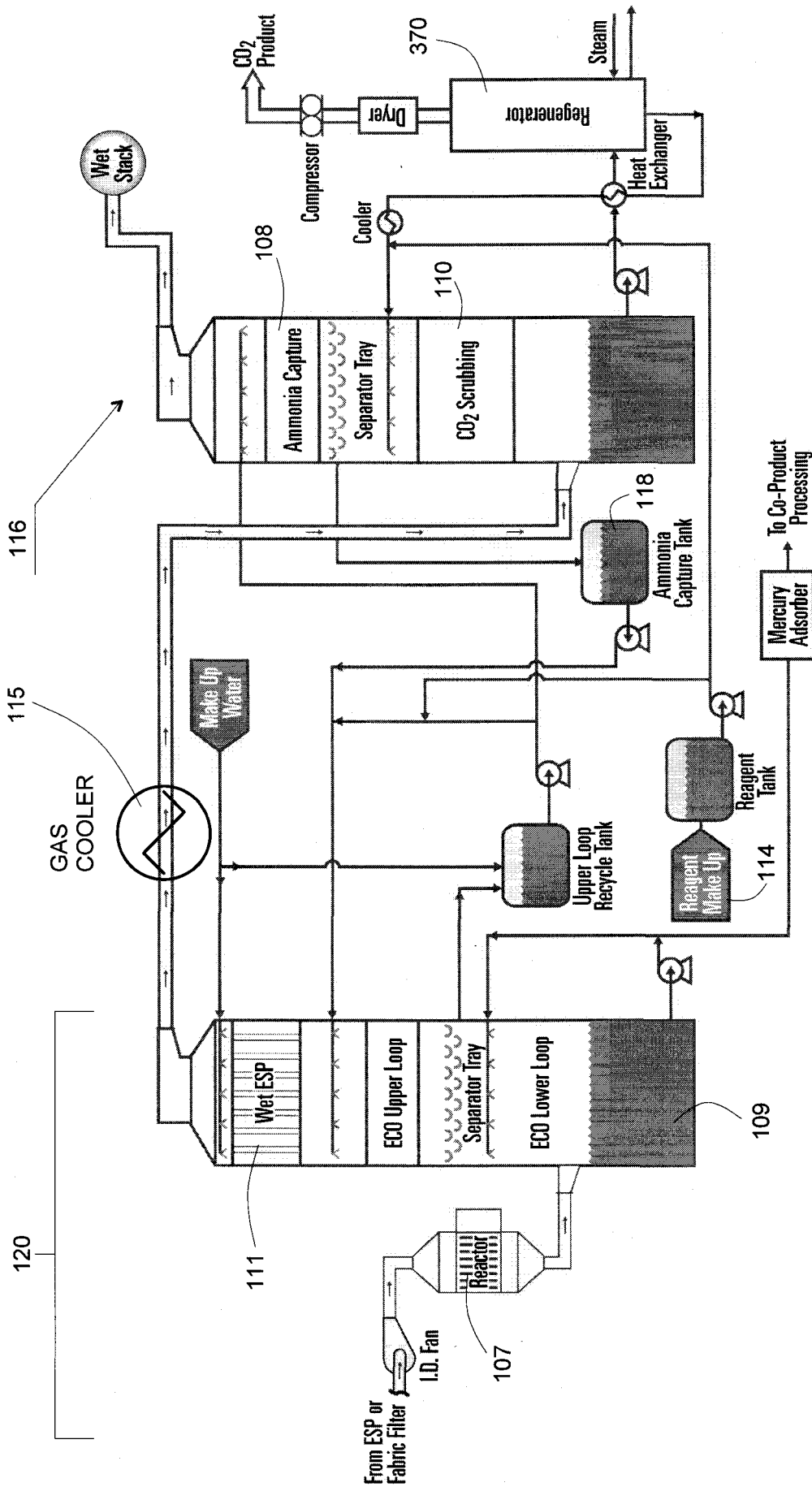


Fig. 2. Incorporation of the present scrubbing process with the '263 or '231 process



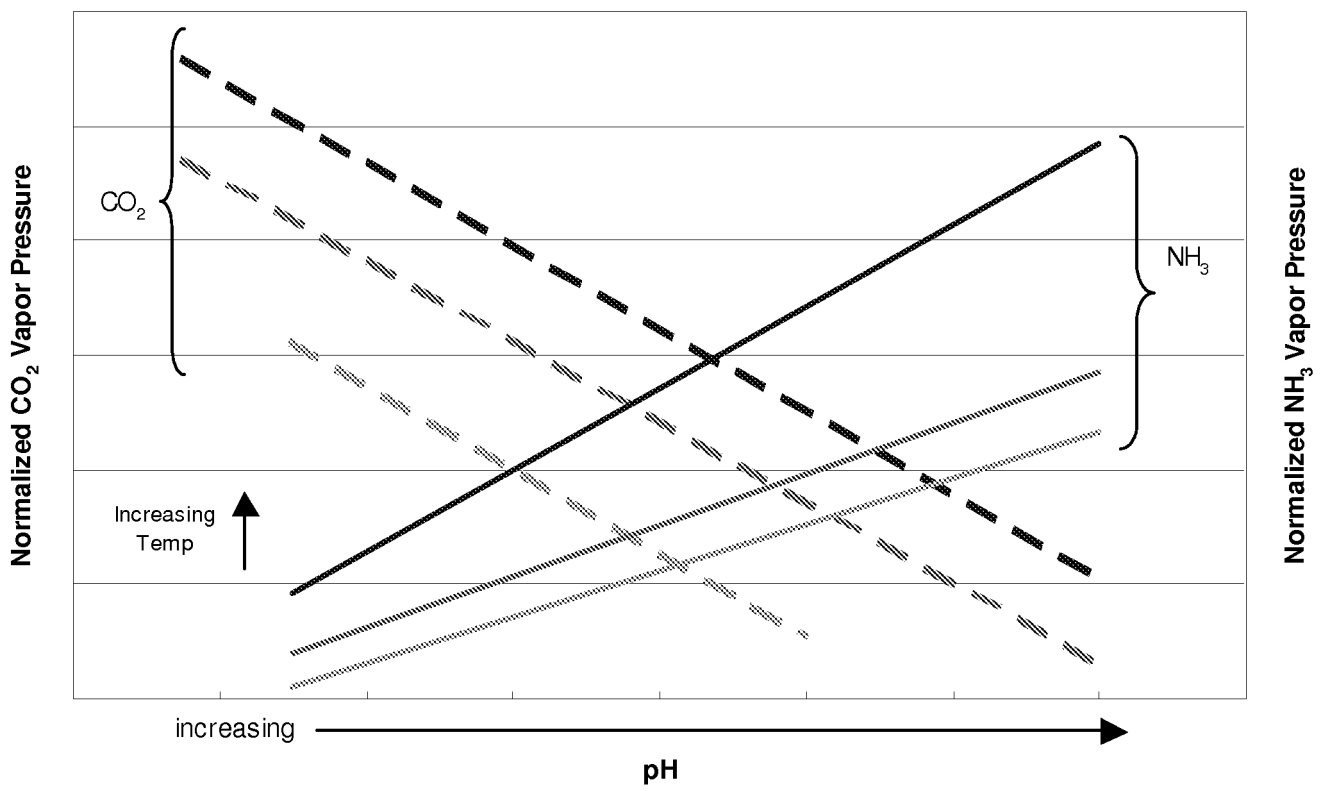


Fig. 3. Equilibrium ammonia and CO2 vapor pressure under absorber conditions

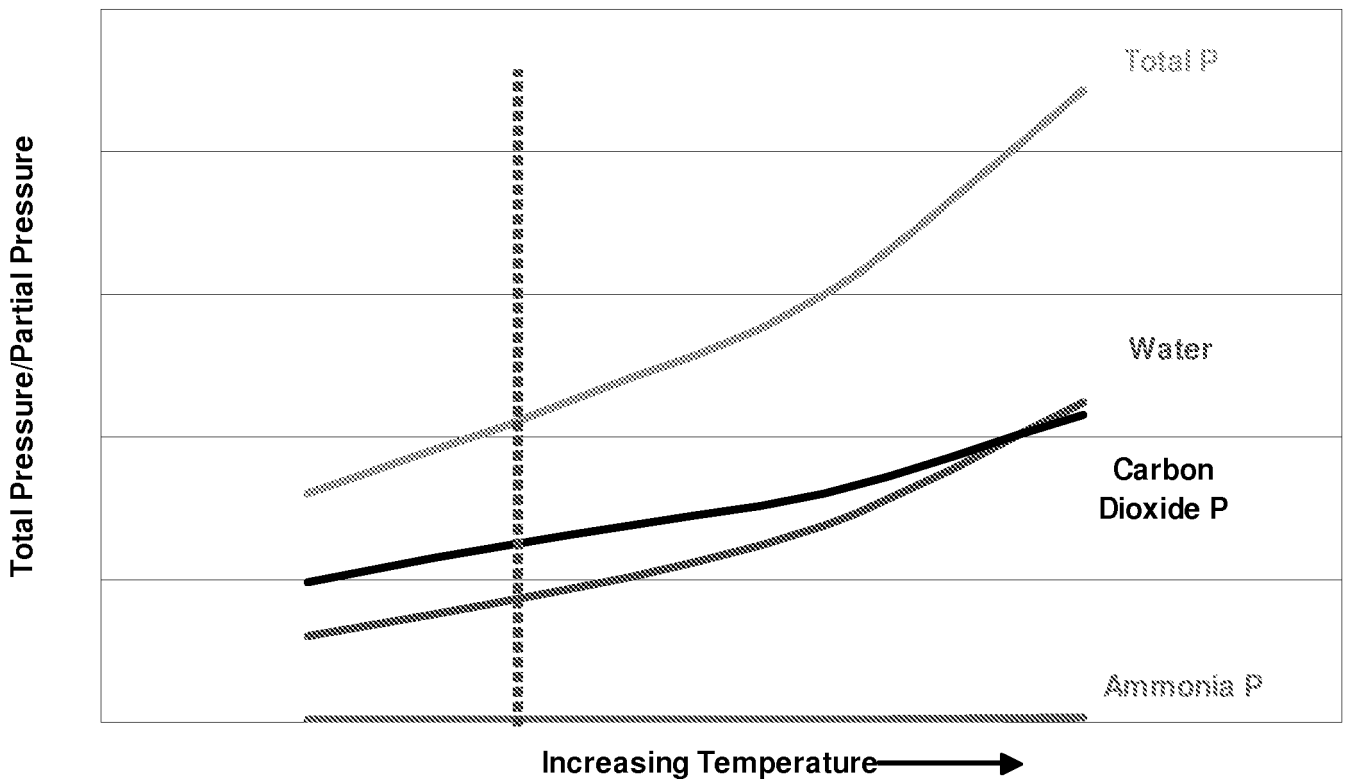


Fig. 4. Effect of temperature on solution regeneration

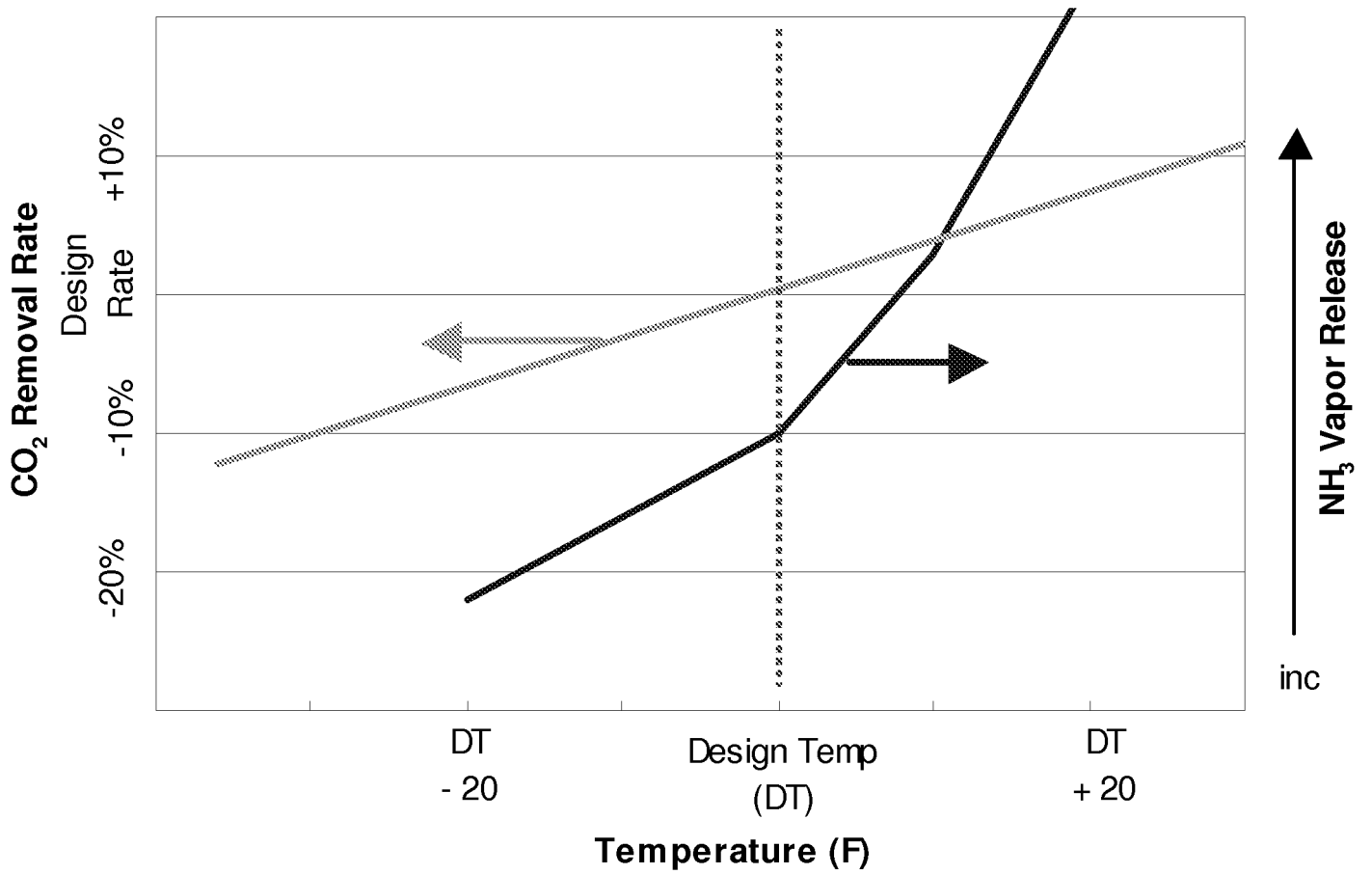


Fig. 5. Effect of temperature on CO<sub>2</sub> absorption and ammonia release rates

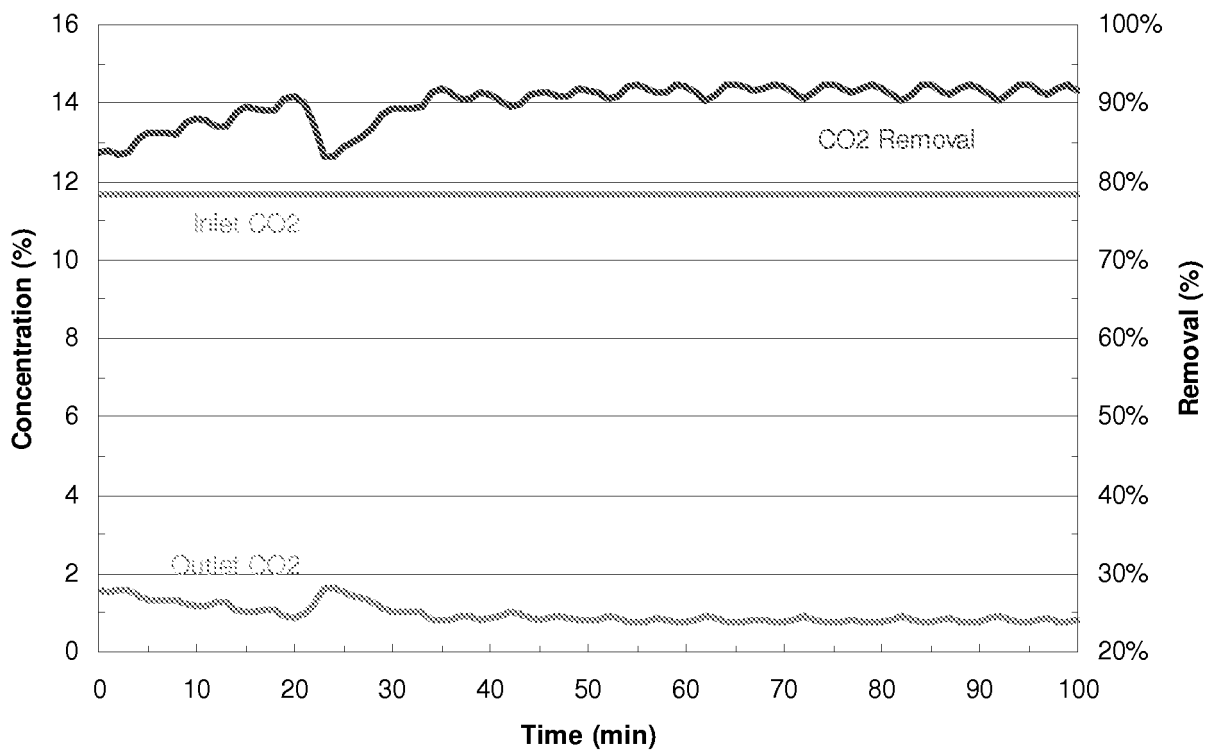


Fig. 6. Steady state absorption performance in lab scale absorption/regeneration system

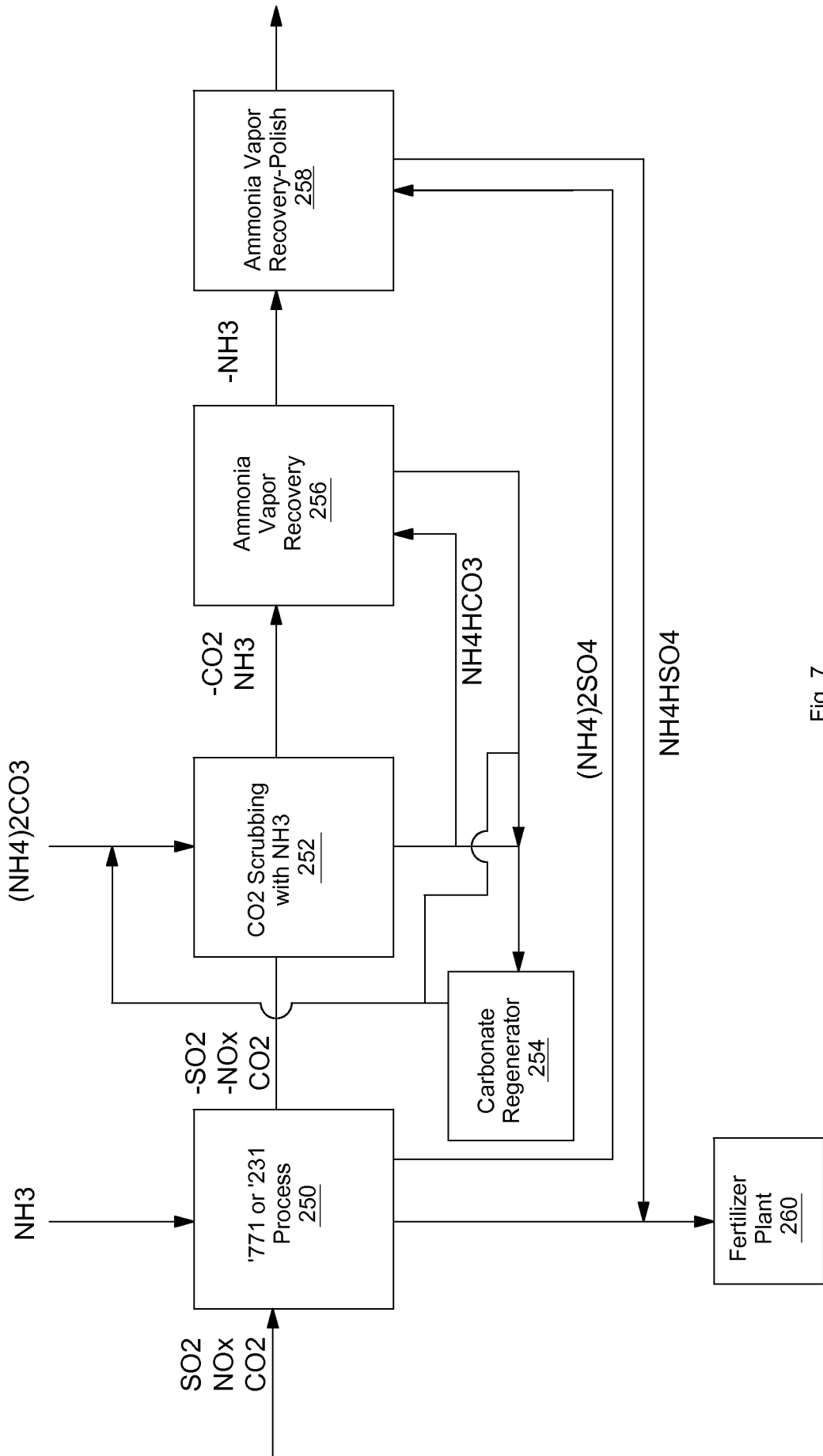


Fig. 7

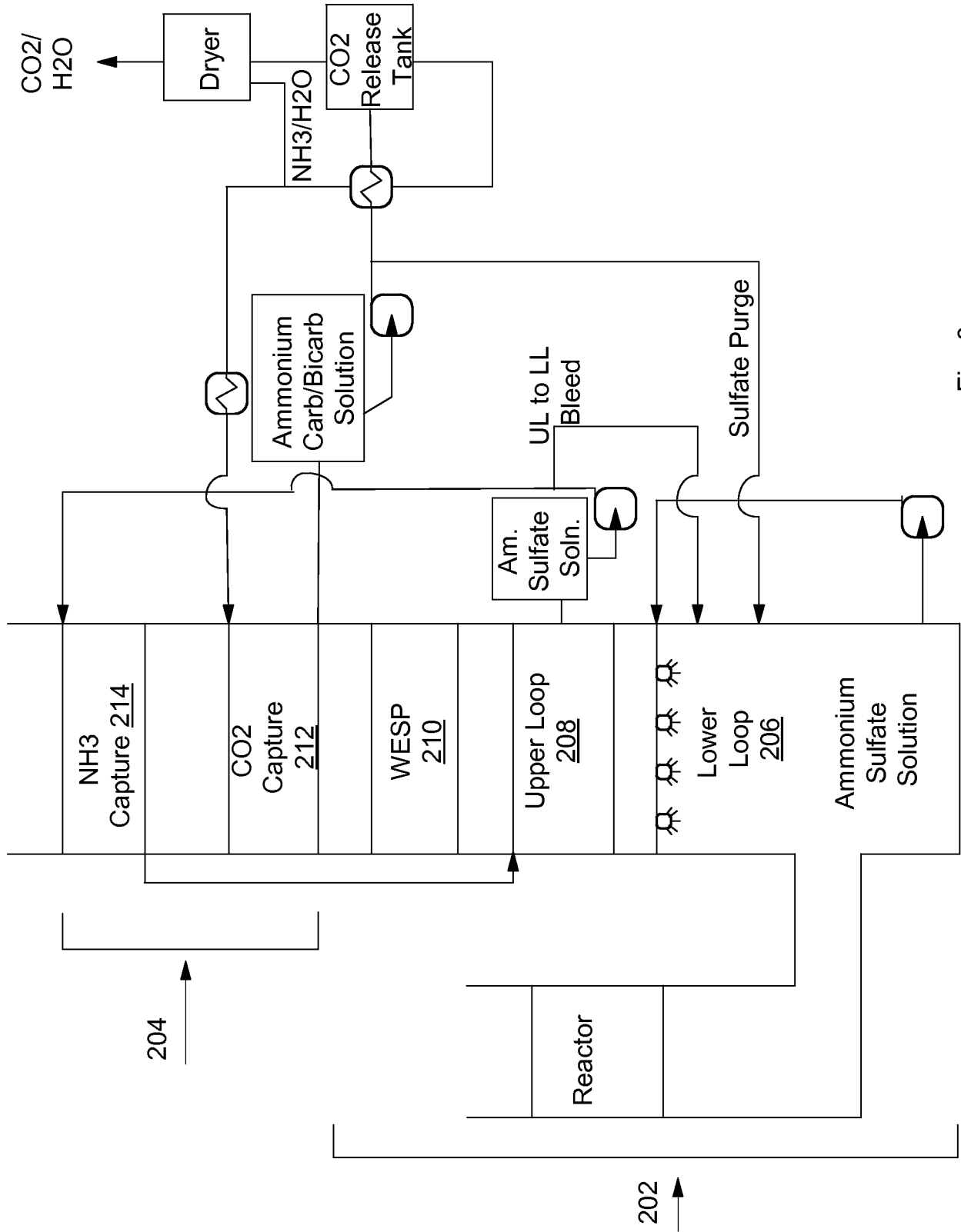


Fig. 8

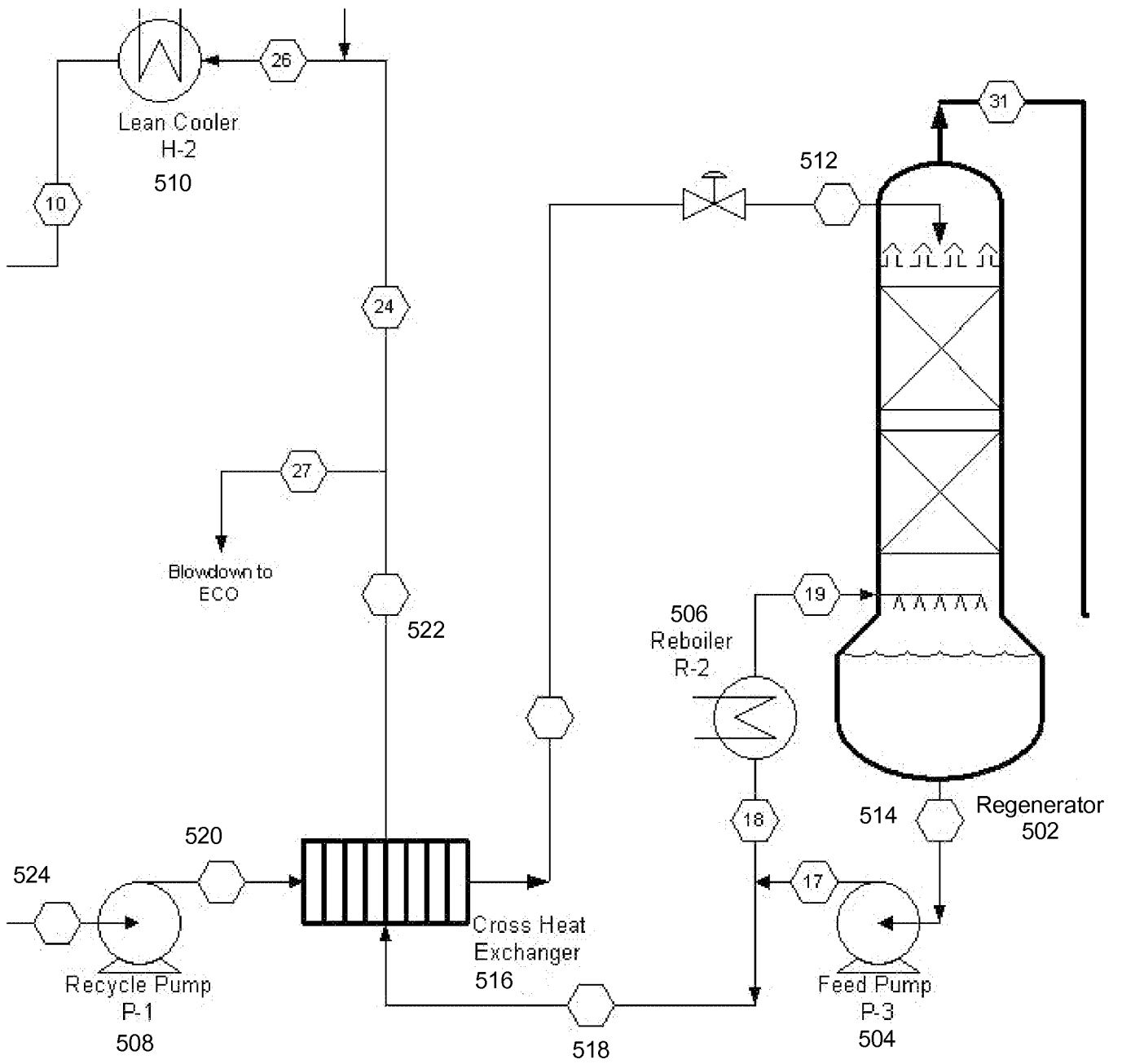


Fig. 8A

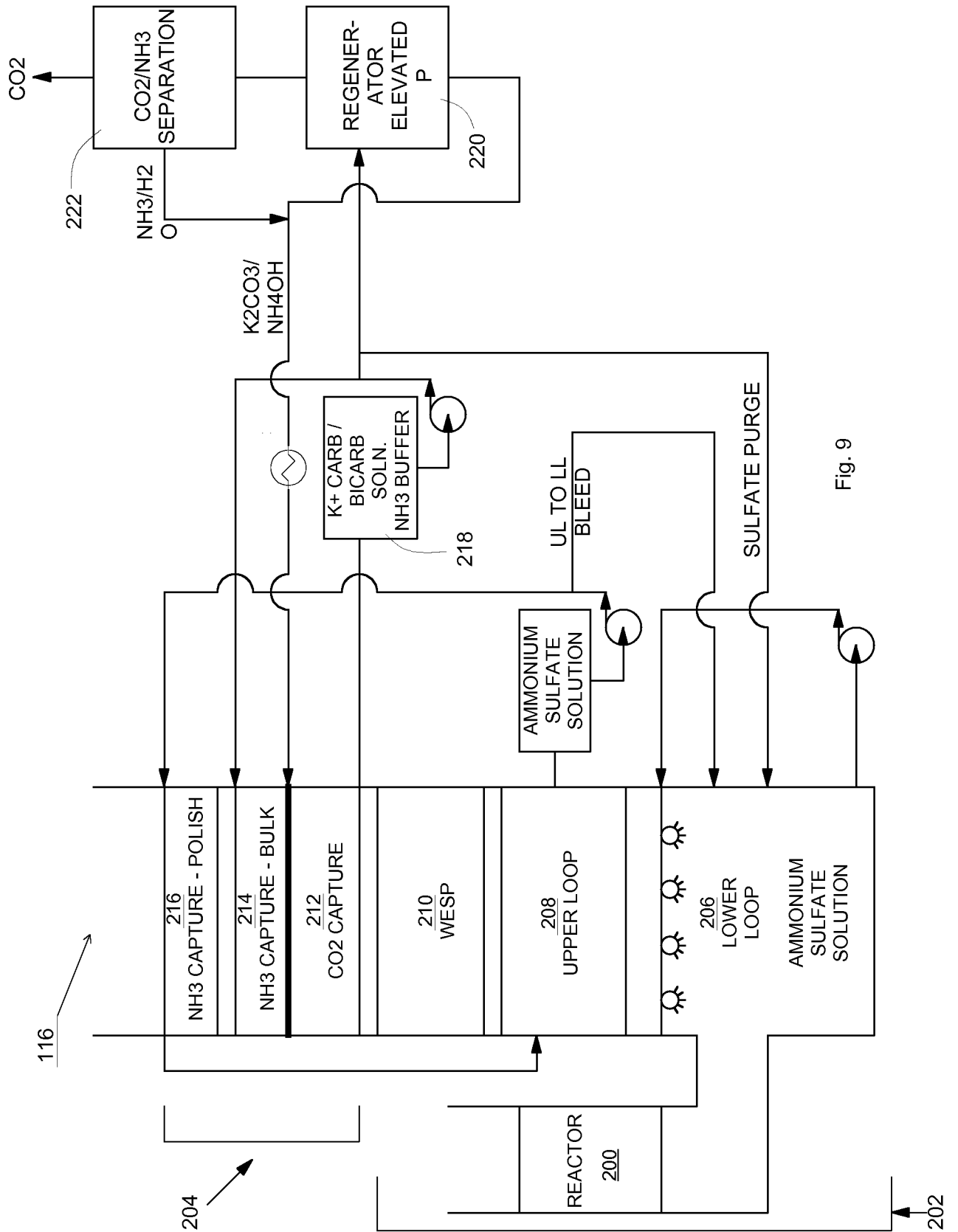


Fig. 9



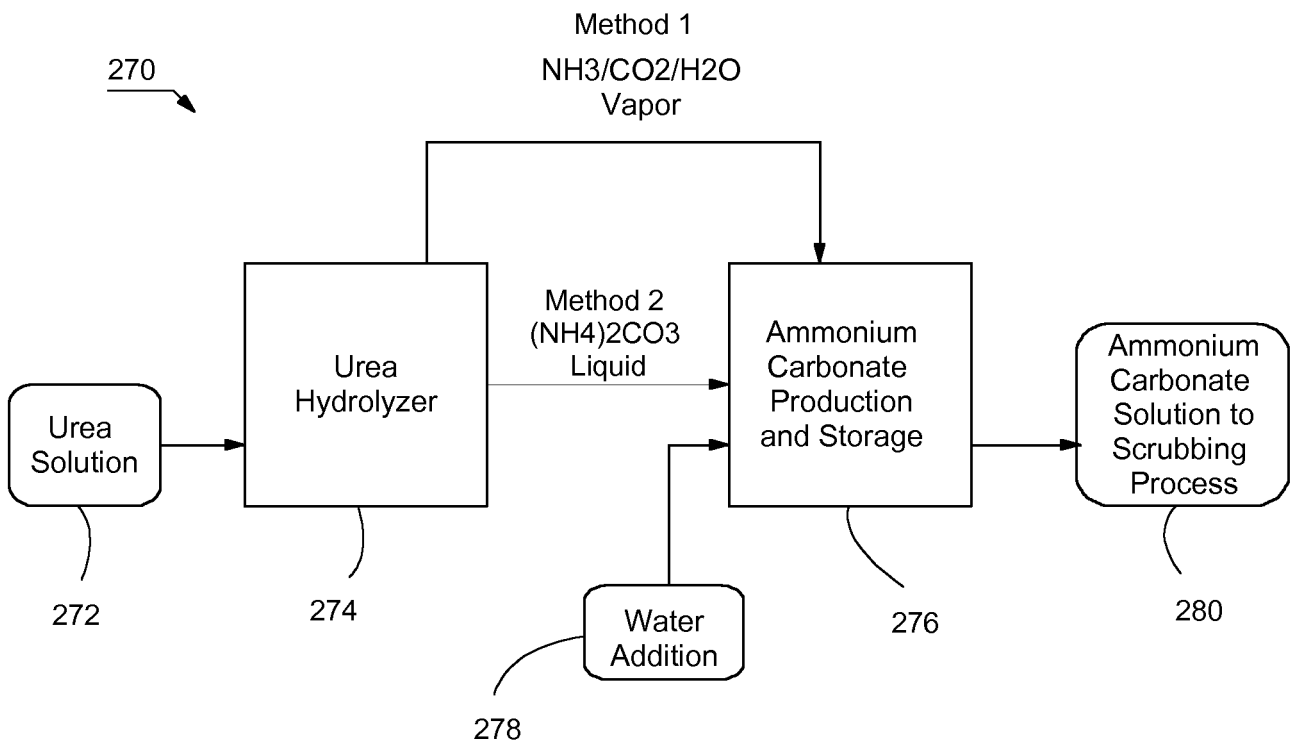


Fig. 10

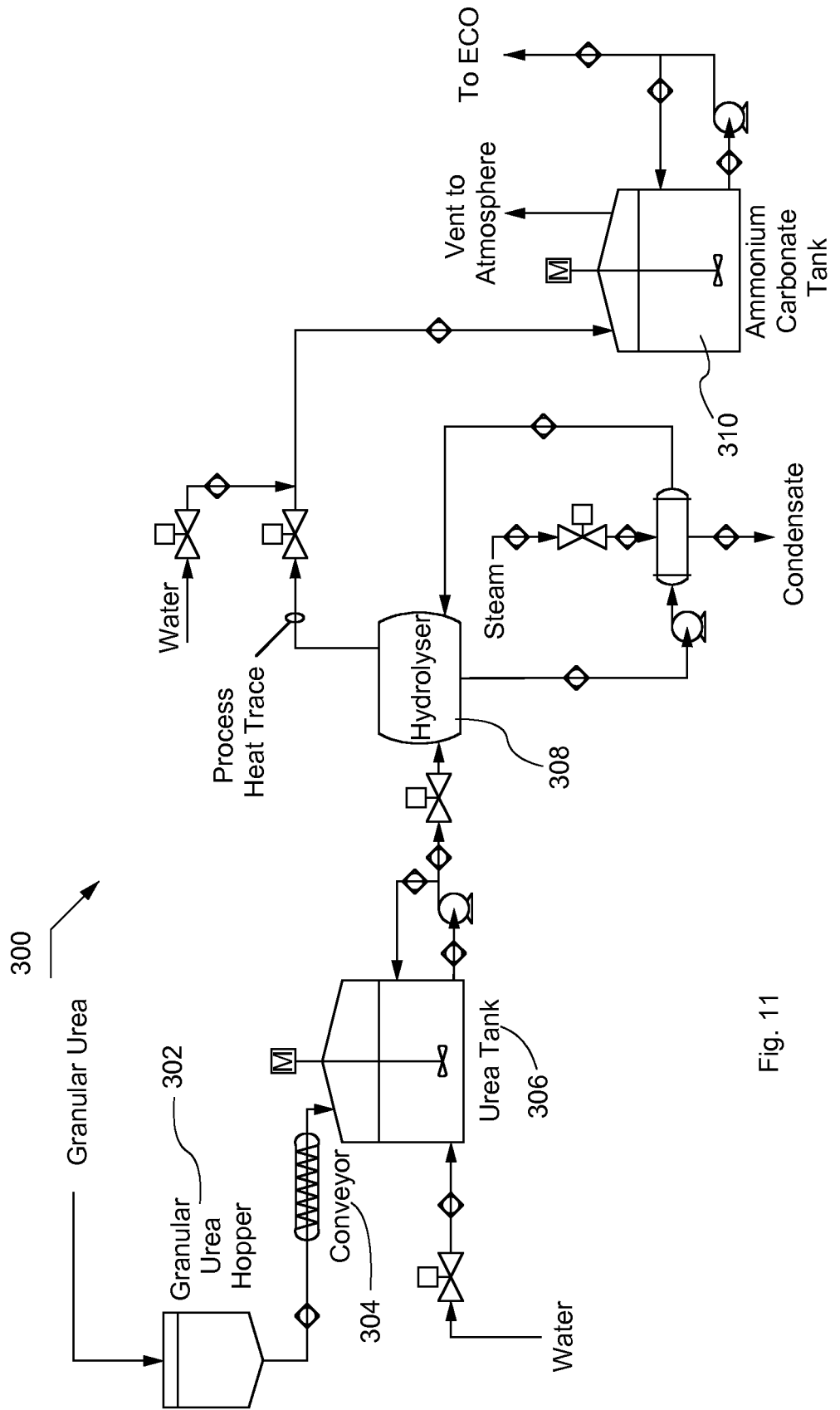


Fig. 11

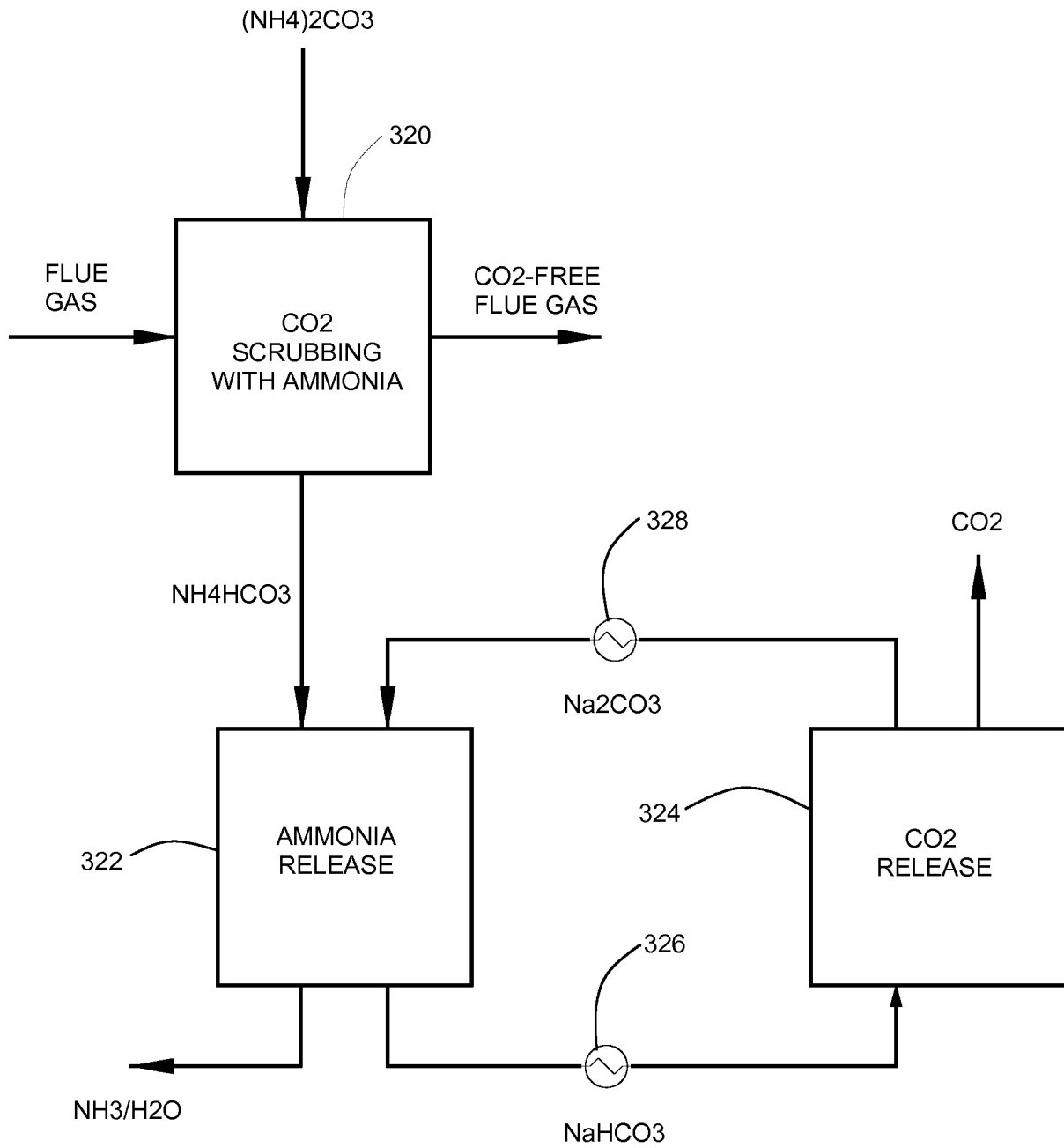


FIG. 12

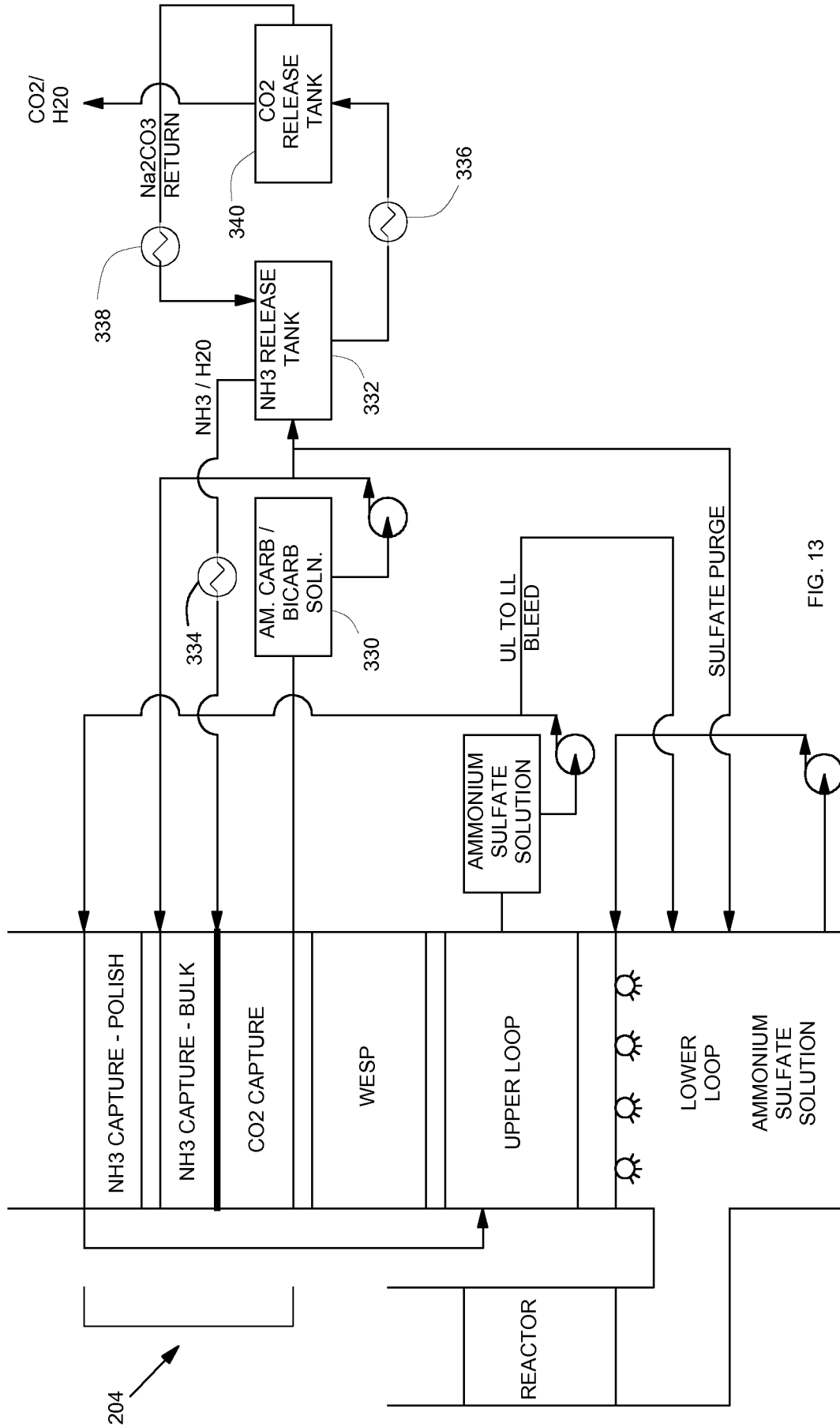


FIG. 13

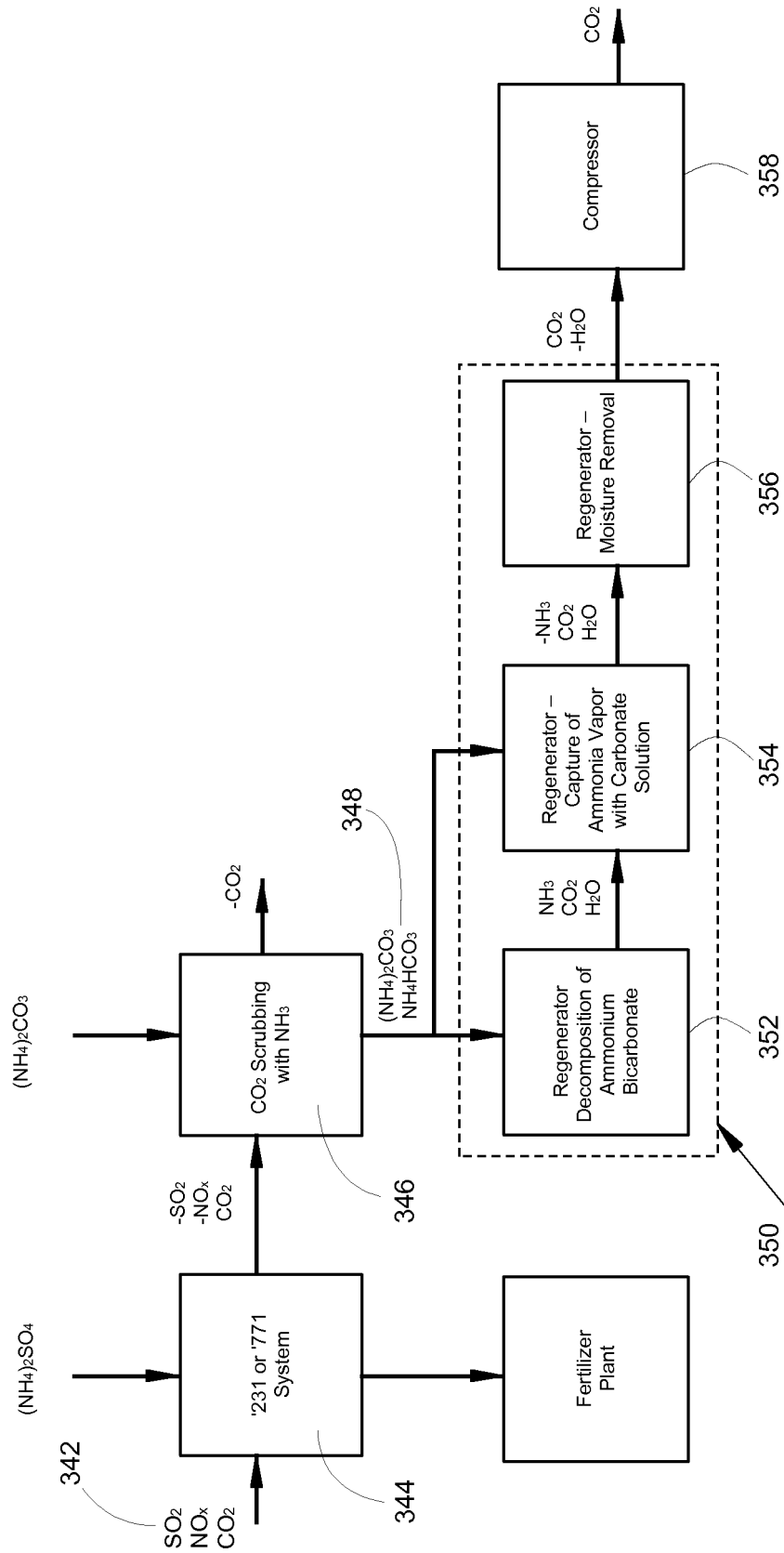


Fig. 14

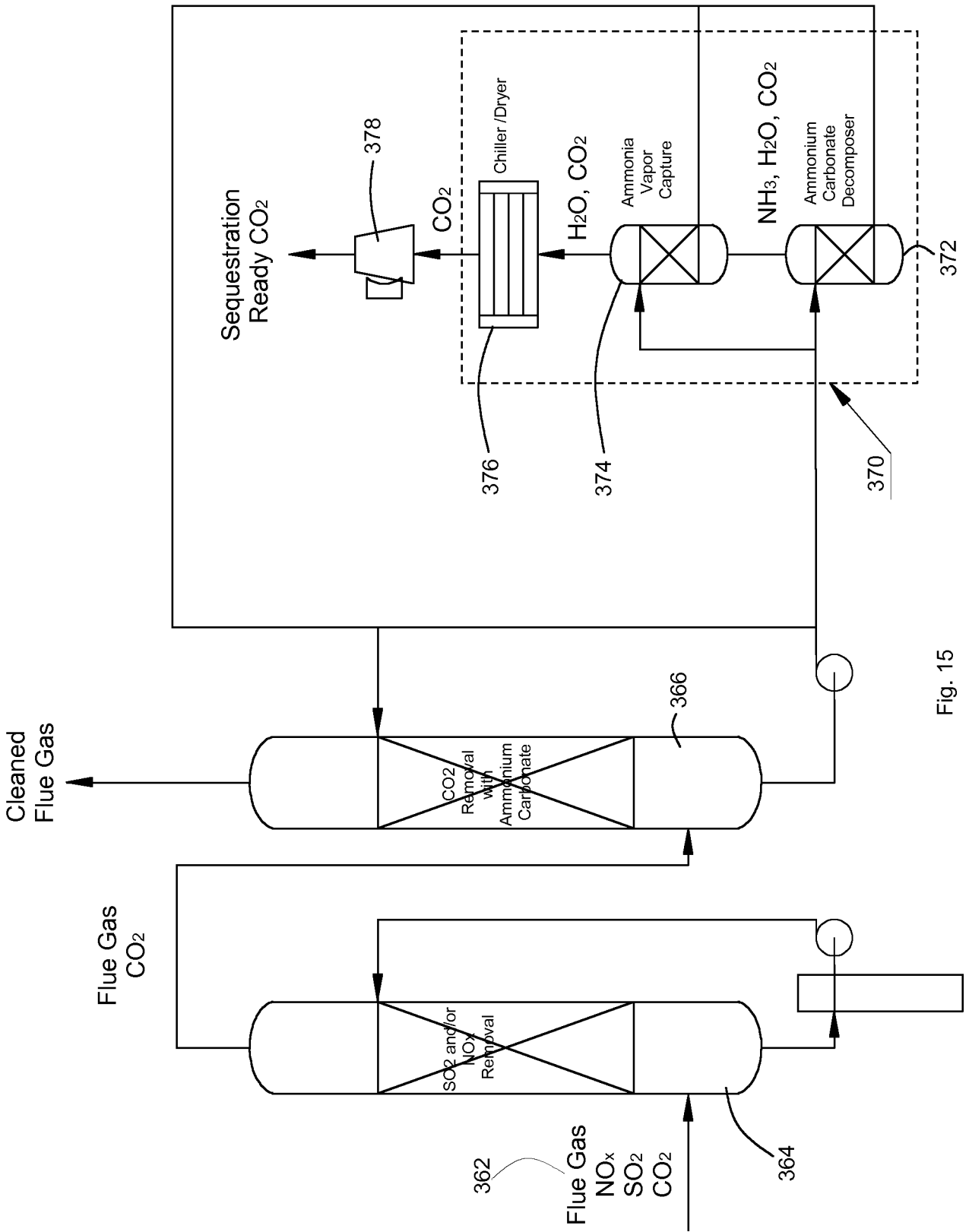


Fig. 15

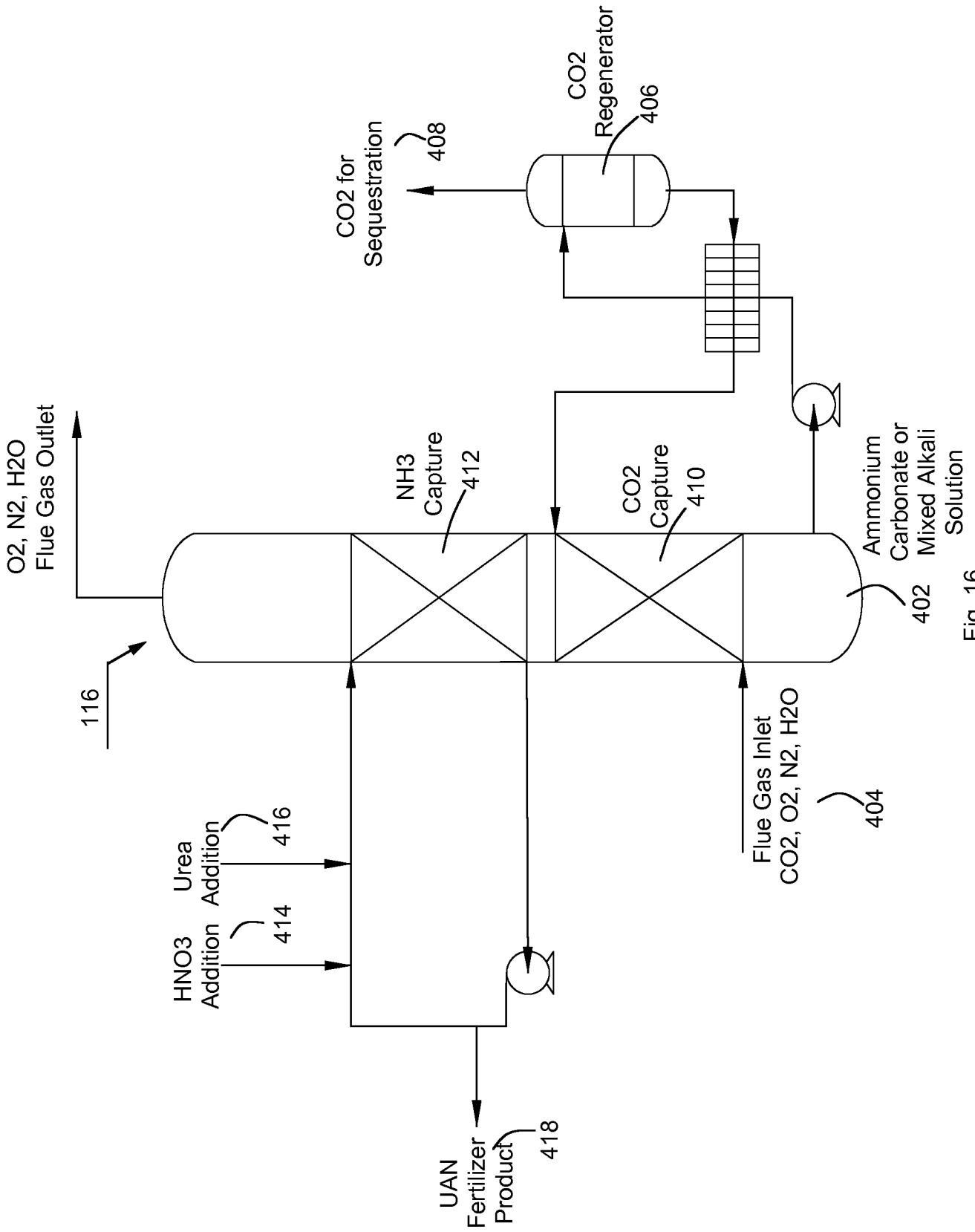


Fig. 16

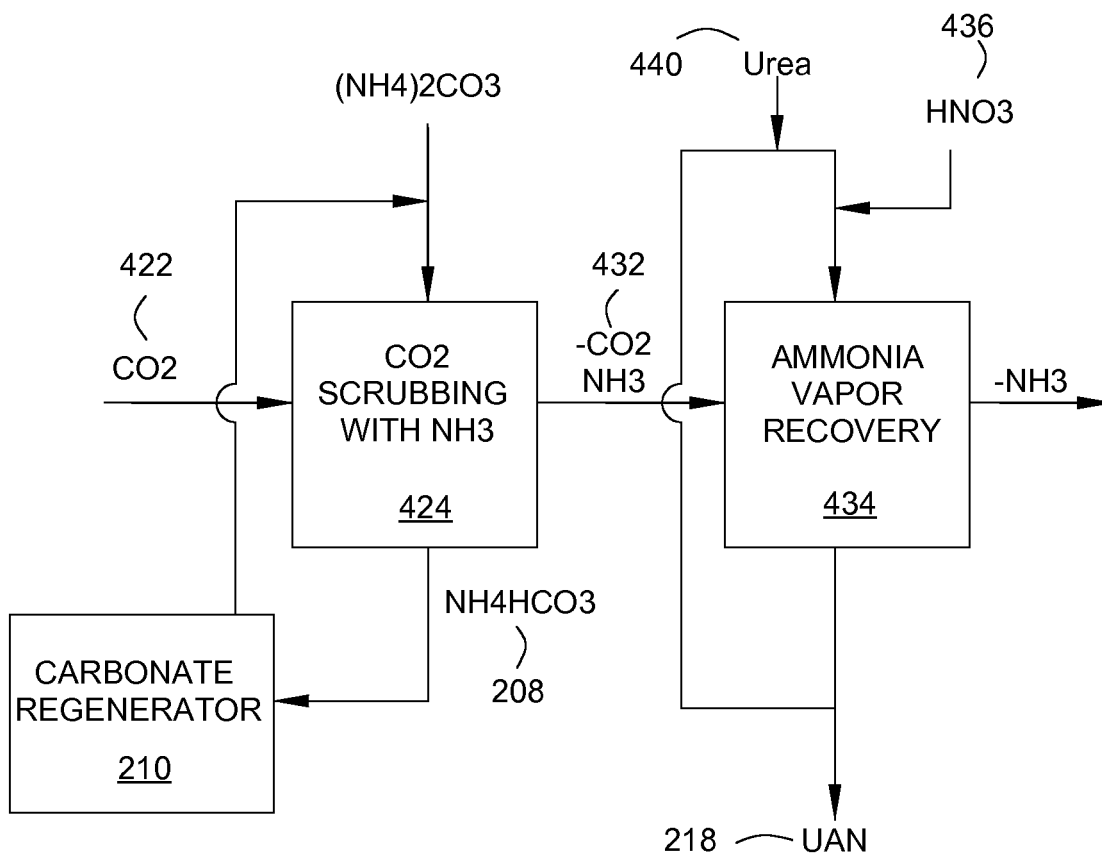


Fig. 17



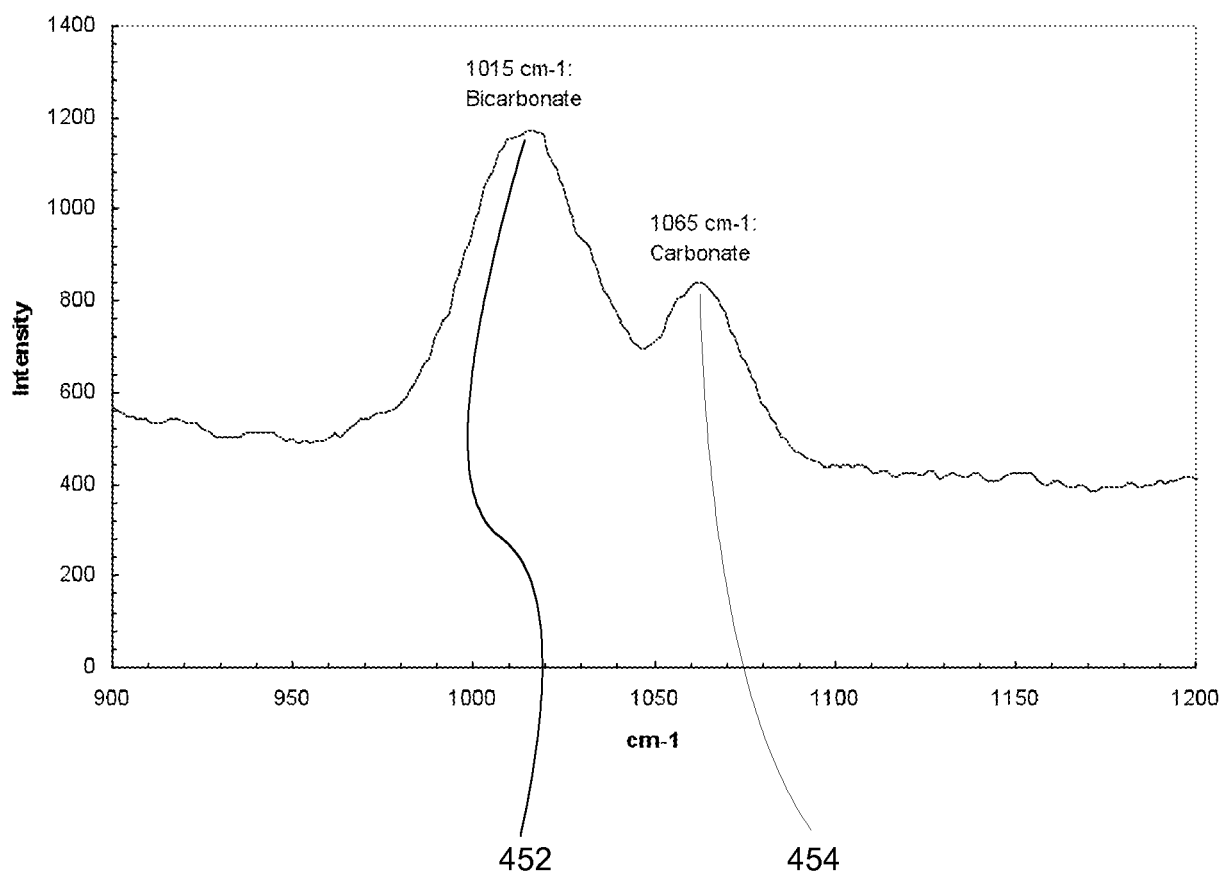


Fig. 17

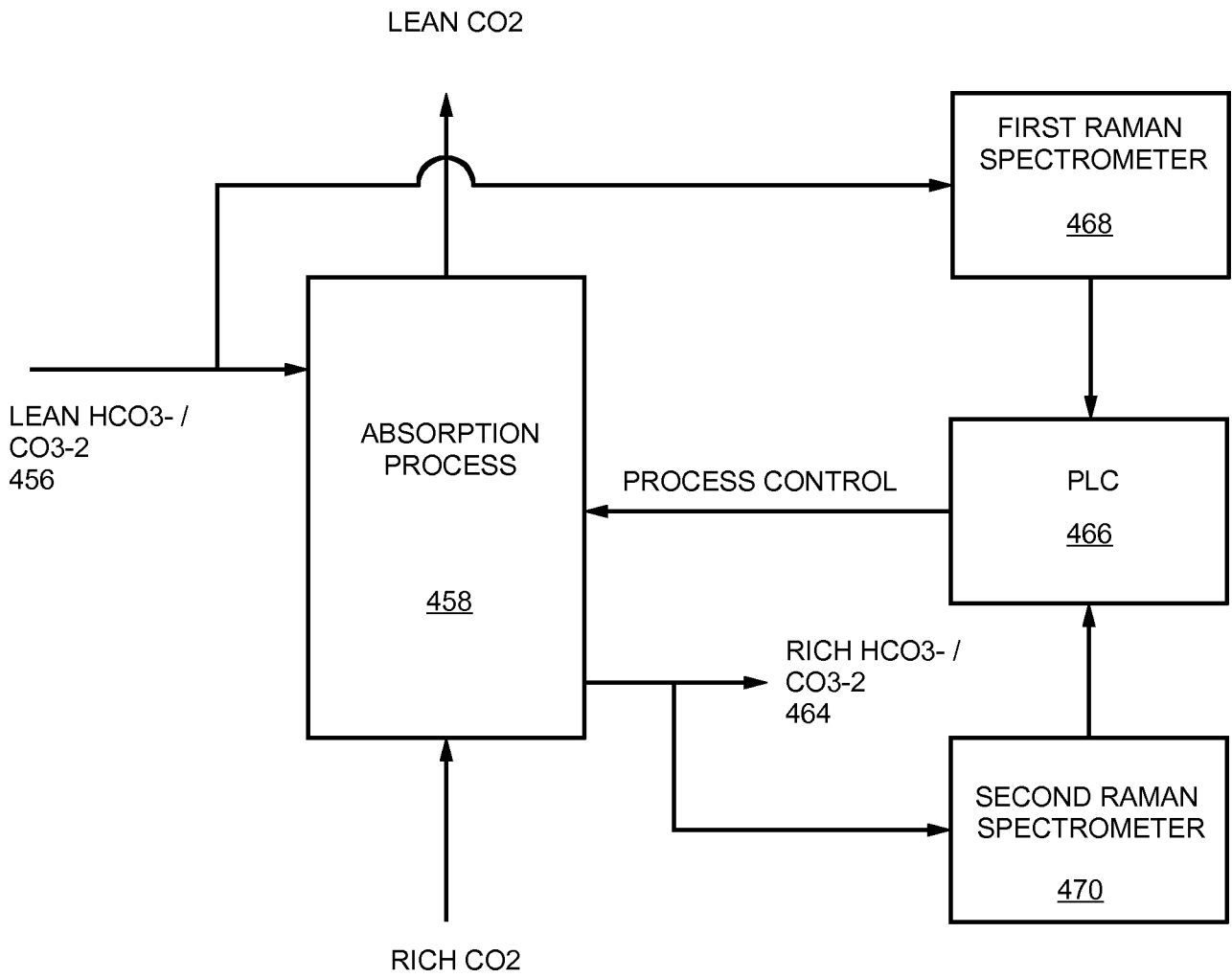


Fig. 19

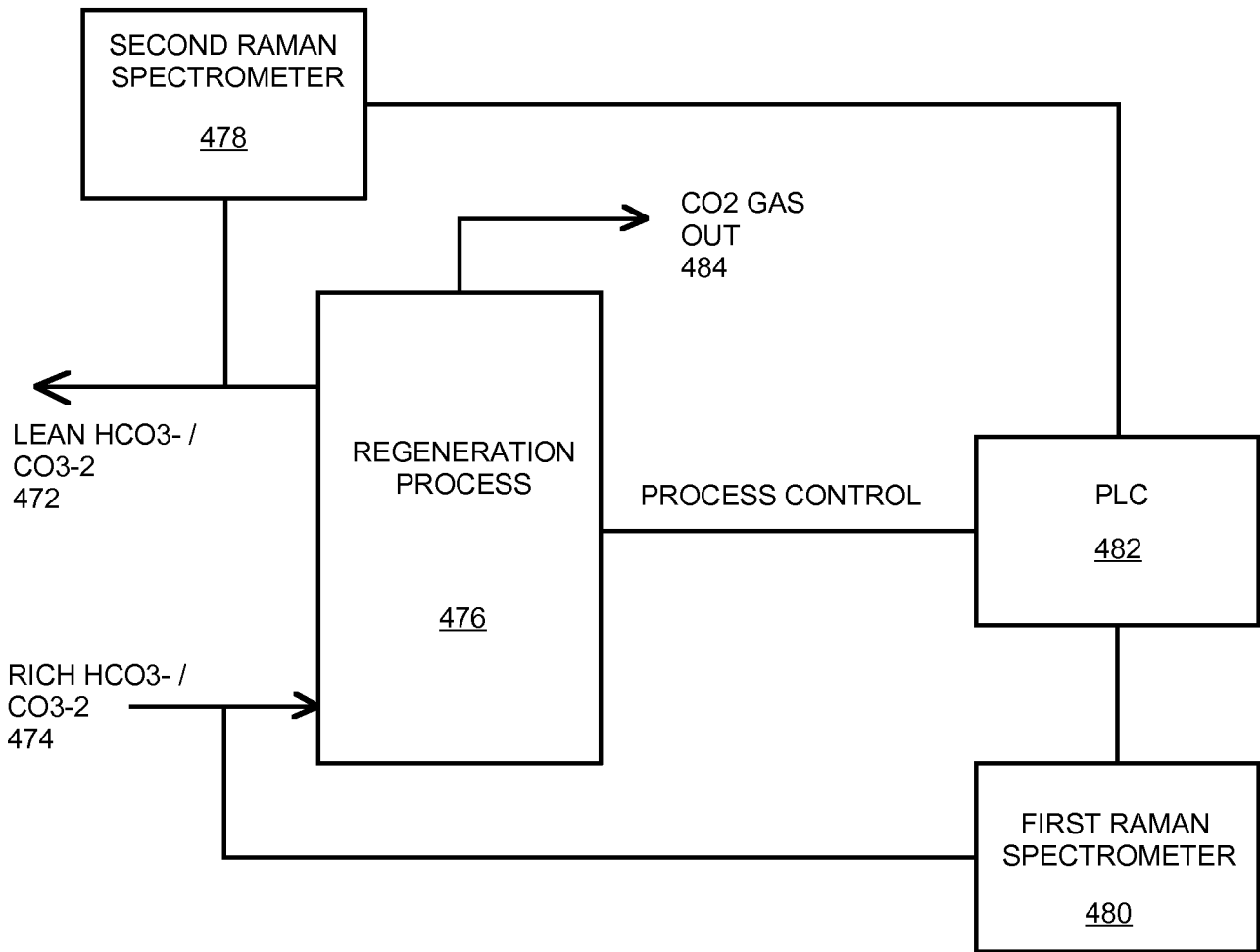


Fig. 20

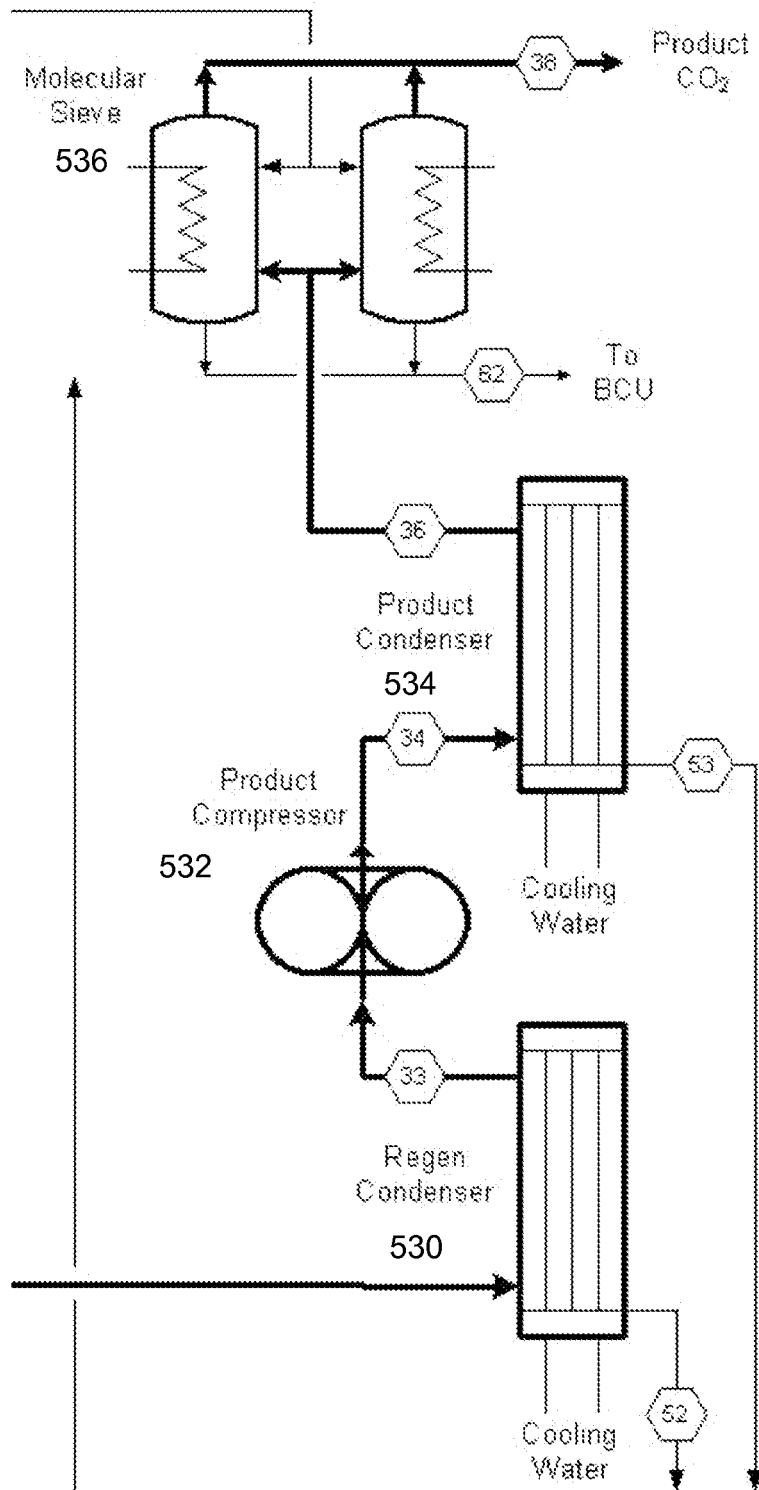


Fig. 21

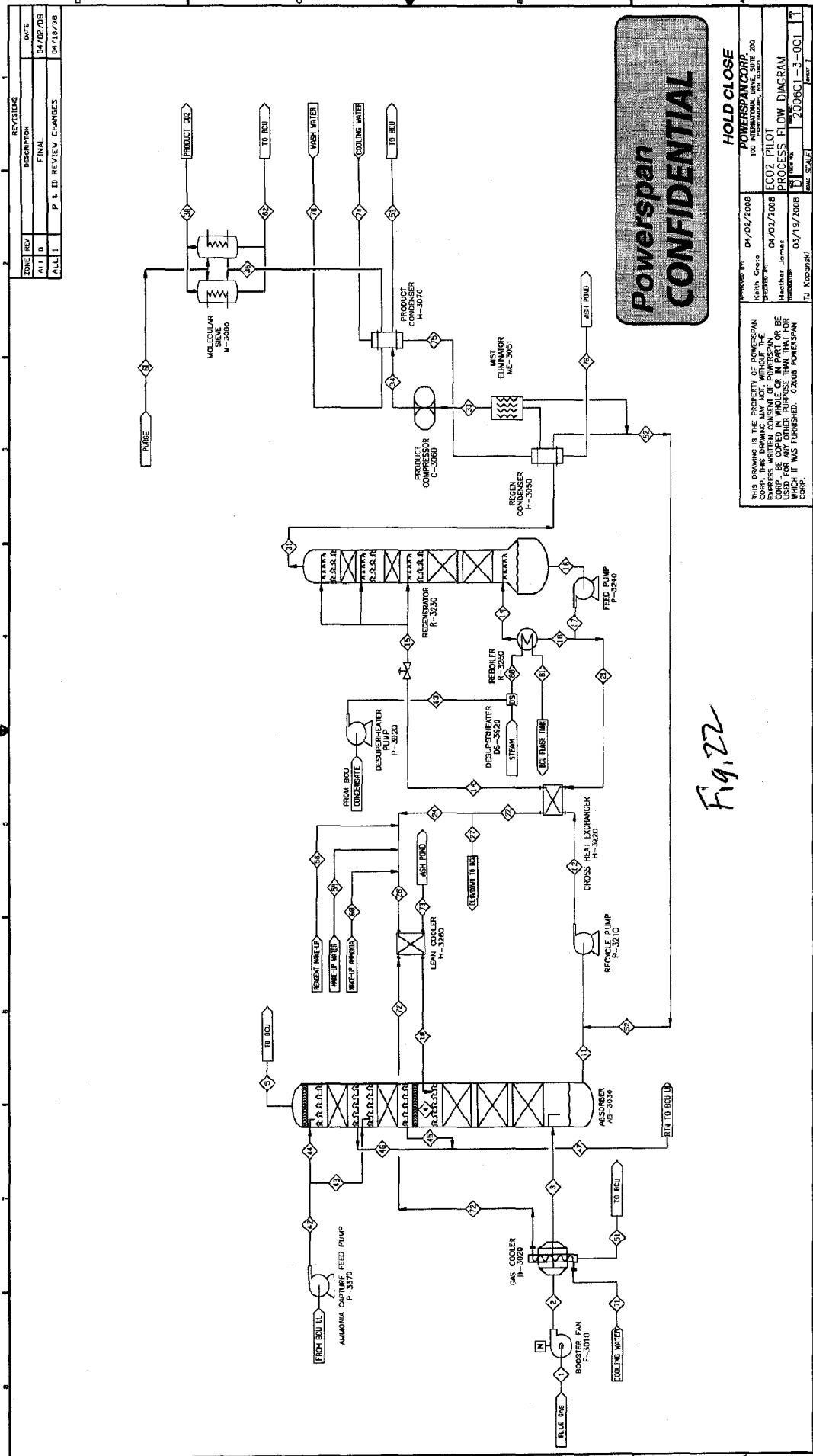


Fig. 22

REVOLUTIONS	
DATE	DESCRIPTION
04/02/08	FINAL
04/19/08	P & ID REVIEW CHANGES
ALL I	

**Powerspan  
CONFIDENTIAL**

<b>HOLD CLOSE</b>	
POWERSPAN CORP. 100 WESTBURY ROAD WESTBURY, NY 09091	
PROJECT NO.	ECO2 PILOT
DATE	04/02/2008
DESIGNED BY	Heather Jones
DATE	03/19/2008
SCALE	AS SHOWN
DATE SCALE	200801-3-001
DATE	03/19/08
BY	TJ Kozlowski

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**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2008/081998

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. B01D53/50      B01D53/62      B01D53/75      C01B31/20      F23J15/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 B01D F23J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 7 255 842 B1 (YEH JAMES T [US] ET AL) 14 August 2007 (2007-08-14) column 1, line 20 - line 31; figure 2; tables 1,2 column 4, line 47 - column 7, line 57 column 8, line 22 - line 29 column 9, line 32 - column 10, line 64 -----	1,2,14, 15 3-13
X	WO 2006/022885 A (GAL ELI [US]) 2 March 2006 (2006-03-02) figures 1,2 page 1, paragraph 3 page 4, paragraph 2 page 11, paragraph 1 - page 14, paragraph 1 ----- -/--	1,14

Further documents are listed in the continuation of Box C.

See patent family annex.

- \* Special categories of cited documents :
- \*A\* document defining the general state of the art which is not considered to be of particular relevance
  - \*E\* earlier document but published on or after the international filing date
  - \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - \*O\* document referring to an oral disclosure, use, exhibition or other means
  - \*P\* document published prior to the international filing date but later than the priority date claimed
  - \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  - \* & \* document member of the same patent family

Date of the actual completion of the international search  
  
**9 February 2009**

Date of mailing of the international search report  
  
**27/04/2009**

Name and mailing address of the ISA/  
 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer  
  
**Burkhardt, Thorsten**

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2008/081998

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 936 231 B2 (DUNCAN JOANNA L [US] ET AL) 30 August 2005 (2005-08-30) cited in the application figure 1 column 3, line 3 - column 6, line 13 -----	3-13
Y	US 6 605 263 B2 (ALIX FRANCIS R [US] ET AL) 12 August 2003 (2003-08-12) cited in the application figure 1 column 2, line 59 - column 5, line 5 -----	3-13
P,A	US 2008/178733 A1 (GAL ELI [US]) 31 July 2008 (2008-07-31) figures 1-3 paragraphs [0033] - [0039], [0049] - [0054], [0057], [0060], [0061], [0066] - [0068] -----	1,3,14

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2008/081998

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

see additional sheet

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.



**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15

An apparatus and a method for purifying gas streams in several steps by removing SO<sub>x</sub>, NO<sub>x</sub>, CO<sub>2</sub> and other impurities with different solvents, i.e. ammonia compounds or alkali carbonates as solvent. Integration between these steps (recycle streams). Aspects of control and of heat integration.

---

2. claims: 20-22

An analytical method to determine the bicarbonate/carbonate concentration, preferentially in a CO<sub>2</sub> absorption process, by means of laser light or Raman spectrometers.

---

3. claims: 16-19,23

CO<sub>2</sub> removal from a gas stream by condensation and compression

---

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2008/081998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7255842	B1	14-08-2007	NONE
WO 2006022885	A	02-03-2006	AU 2005278126 A1 02-03-2006
			BR PI0514141 A 27-05-2008
			CA 2574633 A1 02-03-2006
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